UNITED STATES MINERAL RESOURCES

GEOLOGICAL SURVEY PROFESSIONAL PAPER 820

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DONALD A. BROBST and WALDEN P. PRATT, *Editors*

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ROGERS C. B. MORTON, *Secretary*

GEOLOGICAL SURVEY

V. E. McKelvey, *Director*

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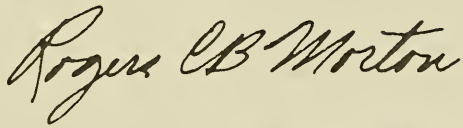
FOREWORD

Minerals and mineral fuels are literally the cornerstones of modern life. They constitute the source materials for most of the things we use, and they supply the energy that powers our machines and heats and cools the air where we live and work. In short, they are the physical source of most of the necessities, conveniences, and comforts of life in the United States today.

Most mineral resources are nonrenewable, for the deposits from which they are extracted are not being naturally reformed at any where near the rate we are using them. They are extendable, however, in the sense that new deposits are discovered by exploration, and deposits once too poor in quality to recover economically are made available by advancing technology. And, of course, many mineral products can be recycled.

Because of our dependence on minerals and mineral fuels, the question of the magnitude of usable resources is of mounting concern. Generally the problem has been assessed in terms of proved reserves—workable deposits that have already been discovered and inventoried. To plan our future, however, we need some idea of the magnitude of resources that are geologically available if we are able to find and use them economically.

As a part of our response to the Mining and Mineral Policy Act of 1970, the Geological Survey provides in this volume the first overall assessment of mineral resources since that of the President's Materials Policy Commission in 1952. It goes beyond traditional resource appraisals, which have considered mainly inventoried reserves, to examine the geologic availability of resources that will be needed in future generations. For many minerals, these appraisals are preliminary at best, for not enough is known about their origin, distribution, or the geologic environments favorable for their occurrence to assess their potential now. But at the least they represent a beginning, a take-off from which we can expect to enlarge our knowledge of our mineral-resource endowment with advancing science and exploration.



ROGERS C. B. MORTON
Secretary of the Interior

PREFACE

The work on this volume began in January 1972, but in a broader sense its production began many years ago. The chapters were written by geologists most of whom have had many years of experience studying the geology of mineral deposits, and more particularly the commodities about which they have written here. A total of nearly 2,300 man-years of professional experience in the geology of mineral resources is represented by the authors of the volume, and about 30 man-years went directly into its preparation. Each chapter contains not only a synthesis of the state of knowledge of the geology of the commodity, but also an appraisal of the known resources, and an examination of the geologic possibilities for finding additional deposits.

In January 1972, responsibility for the preparation of the volume was assigned to us as co-editors, and we were given a tentative list of commodities and authors. We provided each author with a suggested outline of general topics to be covered, and some guidelines as to scope and philosophy of approach, but beyond that we avoided any attempt to fit each chapter into a stereotype. Moreover, the types of commodities range from the major metals and industrial minerals such as copper, silver, and fluorspar, which have been the subject of geologic research for years, to other commodities that are of such varied geologic nature (such as pigments or gemstones) or of such minor present importance (such as scandium or thallium) that they cannot be treated from the same viewpoint as the major minerals. The chapters range, therefore, from comprehensive summary reports to general essays that reflect the individuality of the authors as well as the variation among commodities.

Throughout the book the emphasis is on geology, but each chapter contains some summary information on uses, technology, and economics. These summaries are not meant to be exhaustive, however, and additional details are in the 1970 edition of "Mineral Facts and Problems" (Bulletin 650 of the U.S. Bureau of Mines); indeed, we regard that book and the present volume as being complementary.

In the examination of the geologic possibilities for finding new deposits—in many respects the principal innovative contributions of this volume—we asked the authors to frankly apply the limits of their ingenuity and not only to summarize current theories but also to express their own intuitive ideas, however speculative and unconventional they may seem, that have come from years of study devoted to the origin of mineral deposits. Readers will see that some authors have speculated more courageously than others. In any case, we believe readers will find all the chapters interesting, and many stimulating; and a few we believe can be frankly characterized as intellectually exciting.

Most chapters include a section on prospecting techniques, and a summary of geologic or related problems on which the authors believe research might be most fruitful in the continuing efforts to find new resources.

An integral part of the book is the bibliographic material cited at the conclusion of each chapter, in lieu of repetition of detailed descriptions already in print. Index and "spot" maps are not included in most chapters because they are available elsewhere, and in many cases with more detail than could possibly be included here. Maps showing the distribution of known deposits of many commodities in the United States are available in the Mineral Resource (MR) map series of the U.S. Geological Survey and in the National Atlas of the United States.

The first three chapters deal not with resources of specific commodities but with general information that is pertinent to the study of mineral resources. In the introductory chapter we discuss the purposes of the book, the distinctions between reserves and various categories of resources, and some general conclusions drawn from our view of the book in its entirety. In the second chapter V. E. McKelvey discusses the problems of mineral-resource estimates and public policy. In the third chapter, R. L. Erickson discusses some new points of view on the relation of reserves and resources to the crustal abundance of elements.

We acknowledge with thanks the cooperation of our colleagues in all phases of the preparation of this volume. Whatever success the book may attain is due entirely to a total effort. A paragraph of acknowledgment originally submitted as a part of the chapter on "Nuclear fuels" is given here instead because we feel it applied to all chapters: "The writers have drawn freely from published informa-

tion, not all of which is cited, and from their colleagues, none of whom are given specific credit. The reader should be aware that the paper could not have been written without these sources." We extend specific thanks to Michael Fleischer for preparation of summaries of geochemical information that are included in many chapters.

Donald A. Brobst
Walden P. Pratt

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INTRODUCTION

By Donald A. Brobst and Walden P. Pratt

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THE PURPOSE OF THIS BOOK

Our civilization is dependent on minerals. Few people living in the United States and other developed nations pass through a single day without using raw or manufactured materials that have been been made from, processed by, fertilized with, or in some other way affected by minerals or mineral products. Without a steady supply of minerals our civilization could not survive.

Unlike most other natural resources, minerals are not renewable. They are formed in the earth's crust by infinitesimally slow natural geologic processes acting for thousands or millions of years. Once removed and used, they cannot be grown again. The vital question, then, is this: Is our supply of minerals running out?

To answer this question, as it applies to nearly all the mineral commodities in use today, is the general aim of this book. More specifically, the book attempts to provide answers to three basic questions about each mineral commodity: (1) How important is it to our present industrial civilization and standard of living? (2) how much of it do we have and to what extent is it economically and technologically available? and (3) how and where can we find more? The emphasis here is on domestic resources, but many chapters include information on foreign resources, generally most complete for those commodities for which we are most dependent upon sources abroad.

The answers to the above questions are matters that should be of concern not only to geologists (both professional and student), but also to exploration managers, research administrators, economists and economic analysts, legislators, lawyers, planners, magazine and newspaper editors, and indeed many segments of the public at large. The book has been written with this varied audience in mind. The descriptions of the geology and origin of mineral deposits in each chapter necessarily involve some scientific jargon, but discussions of the uses, importance, history of exploitation, resources, and problems needing research are cast largely in nontechnical language so that they may be of use to scientist and nonscientist alike.

RESOURCES OR RESERVES?

A fundamental concept in the evaluation of mineral resources is the distinction between *resources* and *reserves*. Detailed definitions vary (the entire problem of resource terminology is currently being

studied by the National Commission on Materials Policy), but the principal distinction is based on current economic availability: *reserves* are *known, identified deposits* of mineral-bearing rock from which the mineral or minerals can be extracted *profitably with existing technology and under present economic conditions*; whereas *resources* include not only reserves but also other mineral deposits that may eventually become available—either known deposits that are not economically or technologically recoverable at present, or unknown deposits, rich or lean, that may be inferred to exist but have not yet been discovered. A simple analogy from the field of personal finance, suggested by our colleague J. E. Gair, may be helpful in clarifying this important distinction: *Reserves* are represented by the funds in one's bank account and by other liquid assets; *resources* then include, in addition, all other assets and, more importantly, all income one may expect to receive, from whatever source, through the duration of one's lifetime. We will discuss various categories of resources and their relation to reserves later in this introduction, but for the present we would emphasize that because reserves are the only part of the total resource that is *immediately available*, they are of paramount concern to the mineral industry, and reserve estimates for most mineral commodities are generally available and are undergoing constant revision. For most minerals, however, current reserves are only a small part of the total resource. The remainder of the total—the *potential resources*—are by far the most important for the long term, and they receive major emphasis in this book. Mineral resources, whether real or potential, are geologic entities—concentrations of one or more elements in the earth's crust. Because such concentrations occur as the result of geologic processes, the question of how and where to find more of them can ultimately be resolved only through the understanding of geologic principles and the application of geologic insight; accordingly, the chapters of this volume deal with predictions based on geologic reasoning, and have been written by geologists.

A WARNING

Implicit in the distinction between reserves and resources is a serious danger, which we state now and will reiterate throughout this volume: Potential resources are *not* reserves; they are "birds in the bush," or to return to the analogy already used, they are frozen assets and next year's income, and *cannot* be used to pay this month's bills. No matter how optimistic an outlook is engendered by estimates of vast resources, such resources cannot be mined, much less used, until they have been converted into the category of reserves, whether by discovery (of undiscovered resources of minable quality), or by improvements in technology (for recovering identified subeconomic resources), or by both. For nearly all minerals, the estimates of potential resources indicate quantities that may become available *only if we vigorously pursue geologic and technologic research* to discover new mineral deposits in regions and geologic environments that are known to be favorable, to discover new favorable regions and environments, to discover new kinds of mineral deposits not previously recognized, to improve existing exploration techniques and develop new ones, and to improve extractive technology for processing low-grade ores that are not now economically recoverable. Readers of this volume must therefore be cautioned that the resource estimates contained herein are indeed estimates, not measurements; and they present an optimistic outlook for many commodities *only in the context that they represent a potential, not a reality.* Using these estimates in any effort to optimize our domestic resource outlook may only defeat the purpose if they are removed from this context or are quoted without adequate qualification. We have attempted to insure against such misinterpretation by repeating definitions of the appropriate resource terminology on all tables of resource estimates in this volume.

Even with these qualifiers, some may criticize this volume for its articulation of a philosophy that they may consider to be unrealistic. We can only offer the response that in the fairly recent past, each of the kinds of geologic and technologic research enumerated in the preceding paragraph *has in fact resulted in the conversion of potential resources into minable reserves*—"rock in the box," in mining parlance; a few examples are the discoveries of the huge Kidd Creek zinc-copper-silver ore deposit in Ontario and the disseminated gold deposits of Carlin and Cortez in Nevada, and the development of technology for processing taconite iron ores.

Indeed the events of the last 20 years are the best reason for optimism. In 1952, the recoverable reserves of lead were estimated to be 7.1 million tons, of which only about 1 million tons was called proved reserve. These figures were quoted on page 41 of volume 2 of "Resources for Freedom" (President's Materials Policy Commission, 1952), better known as the Paley report. Farther down on that page we find the following statement, "The poor discovery record of the past few decades provides little basis for optimism that the equivalent of the southeast

Missouri district can be expected to turn up in the future; the major hope lies in the development of some new methods of prospecting, as, for example, methods that would indicate the probability of deposits in the absence of surface ontcrops." Drilling in the mid-1950's on the west side of the Southeast Missouri district resulted in the discovery of the large unexposed deposits of lead ore known as the Viburnum Trend. By 1970, half a dozen mines were operating, and the reserves of lead in Missouri alone had increased to 30 million tons. (See the chapter on "Lead" in this volume.) The Viburnum Trend will yield more lead than the total production of the old part of the district. With the phoenixlike rejuvenation of the Southeast Missouri district, the Viburnum Trend becomes the perfect example of a potential resource converted to a reserve.

We see no reason why such discoveries and developments cannot be expected to continue in the future. To point the direction to potential resources and to attempt to evaluate them are the objectives of this book.

OUR DEPENDENCE ON MINERALS

Few people are fully aware of their daily dependence upon minerals. An awareness is growing as the fragilities of modern civilization, stemming from population growth and economic expansion, become recognizable not only as world and national problems, but also as personal problems. The availability of mineral resources to meet the projected demands will critically affect future events.

It is important, therefore, to be able to predict the occurrence of minerals, with some degree of realism, on several different scales of both time and space; we must know not only in which direction a particular mine opening should be extended to continue in an ore body, but over a longer time period, we must know where prospecting and exploration should be concentrated to discover new deposits of each kind of mineral—and the likelihood of success. In other words, where are our potential mineral resources and how large are they? How long will they last? For which minerals, if any, are we "in good shape"? Is our supply of any minerals unlimited? Of which ones do we have very little, or are we likely to run out in the near future? For these, is there a geologic probability that more can be discovered in the United States?—that is, are there geologic environments in which such minerals are likely to occur? If so, where? And what problems are likely to be encountered in finding and extracting them? If domestic resources are not likely to be sufficient, then to which parts of the globe must we look for adequate resources in the future? These are the questions to which the authors of this volume have addressed themselves.

CLASSIFICATION OF RESOURCES

What, then, is a mineral resource? To begin with, we may define a mineral resource as a concentration of elements in a particular location in or on the earth's crust (or, now, also in the oceans), in such a form that a usable mineral commodity—whether it be an element (such as iron or aluminum), a chemical compound (such as salt or borax), a mineral (such as emerald or asbestos), or a rock (such as marble, coal, or gypsum)—can be extracted from it. The perceptive reader will recognize that such a definition has little practical value if the particular mineral commodity cannot be extracted at a profit. As already suggested, this feasibility of profitable extraction, or economic availability, is one of two parameters that distinguish between resources and reserves; the other parameter is the degree of certainty of existence. These two parameters were originally formulated into a classification of resources by V. E. McKelvey (1972), whose presentation of these concepts is so vital to the philosophy of resources, and whose classification is so important as the cornerstone of the present volume, that we have included his article as the second chapter of this volume. We will summarize McKelvey's resource classification by stating merely that he defines *reserves* as economically recoverable material in identified deposits, and applies the term *resources* to include "deposits not yet discovered as well as identified deposits that cannot be recovered now." The terms *recoverable, paramarginal,* and *submarginal* designate successively lower degrees of economic recoverability; paramarginal resources are defined as low-grade resources that are recoverable at prices as much as 1.5 times those prevailing now, and submarginal resources are those of still lower grade. (See fig. 4, p. 12.)

In this volume we use a similar classification of resources; but because of our conviction that the long-range potential lies in resources that have not yet been discovered, our classification places less emphasis on the definition of various levels of economic recoverability, and more emphasis on evaluating the undiscovered—defining the various degrees of certainty. For the purpose of this volume, we distinguish three different such degrees (fig. 1). *Identified resources* are specific bodies of mineral-bearing rock *whose existence and location are known.* They may or may not be evaluated as to extent and grade. Identified resources include

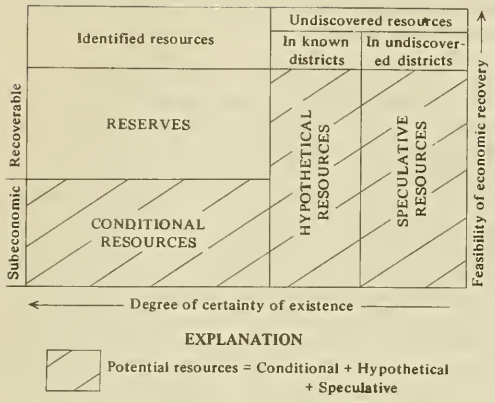

FIGURE 1.—Classification of mineral resources used in this volume.

reserves—masses of rock whose extent and grade are known to a greater or lesser degree and whose grade and physical nature are such that they may be extracted at a profit with existing technology and at present price levels. These last constraints of technology and economics exclude from the category of reserves many mineral deposits that are known and evaluated but are not profitably or technologically minable at present, and to this important category of identified but subeconomic resources we apply the informal term *conditional resources*—resources that may eventually become reserves when conditions of economics or technology are met. Conditional resources have an immediate potential, because they are *known*, and their assessment provides a target for technologic research. This term is used in the volume primarily as a convenience, because most authors were unable to distinguish the paramarginal and submarginal categories in McKelvey's classification.

We divide the remaining potential resources, all undiscovered, into two informally designated categories. *Hypothetical resources* are here defined as undiscovered resources that we may still reasonably expect to find *in known districts; speculative resources* are defined as undiscovered resources that may exist elsewhere—either conventional types of deposits in broad geologic terranes in which as yet there are no discoveries, or else unconventional types of resources that have only recently been recognized (or are yet to be recognized) as having some potential.

The utility of this distinction can be demonstrated by a few examples. In evaluating sandstone-type uranium deposits, for instance, we would consider as *hypothetical resources* the deposits that have so far eluded discovery in the known districts of New Mexico or Wyoming; our geologic knowledge tells us that there is good reason to expect we will find more deposits in those areas similar to the deposits already known, and our estimate of hypothetical resources is, in this case, an attempt to quantify the potential of these undiscovered resources, mainly on the basis of the extent of unexplored but favorable ground. A different kind of geologic perspective, on the other hand, suggests that there is still some likelihood of finding not just new deposits, but new major uranium districts. Our estimate of these *speculative resources*, even though it may be only an order of magnitude, is an attempt to quantify the resource potential of sedimentary basins that are known to exist but have not been sufficiently tested for uranium.

Resources of copper can be used as another example of the distinction between hypothetical and speculative resources. We are justified in *hypothesizing*, for instance, that porphyry copper deposits are concealed under basin fill in and near the known copper districts of the southwest, whereas the discovery in recent years of porphyry-type copper deposits of Paleozoic and Precambrian age in Eastern North America permits us to *speculate* that whole new regions have some potential for new discoveries.

Yet another example of the distinction between hypothetical and speculative resources involves the black bedded deposits of barite such as those currently being mined principally in Nevada and Arkansas. The known deposits are scattered over wide areas of both States, and chances are excellent that new deposits — hypothetical resources — will be found. But recent geologic studies of these deposits suggest that they are related more to sedimentary processes than was formerly believed. If this is true, then the potential for the discovery of new deposits and districts in other sedimentary basins—speculative resources—is likewise excellent. This example is an indication of how the reexamination and study of basic geologic principles can help to open new areas and environments favorable for exploration.

One further aspect of the value of such a distinction is that it has forced us to realize that the speculative resources of some commodities are relatively low. From a worldwide geologic perspective, we can say that the regions with significant potential for discovery of iron, or phosphorite, or marine evaporites, are largely known; thus, the significant undiscovered resources fall under the heading of

"hypothetical," rather than "speculative." For some commodities, this may simply reflect insufficient knowledge of regional geology to identifiy other promising areas, but for others it is an expression of confidence that the favorable terranes have all been identified.

The entire field in the diagram of figure 1 represents our total primary resources (as distinct from secondary resources, such as recycled scrap, which are not considered in this volume)—identified reserves, plus potential resources, which consist of conditional, hypothetical, and speculative resources. Conversions of potential resources into reserves are made by discovery, technologic advance, or changes in economic conditions. The same processes may lead to similar conversions from outside the field—to make potential resources from materials at present inconceivable as resources.

A corollary of the emphasis of this volume on geologic rather than economic factors is that our classification is less concerned with the degrees of feasibility of recovery defined by McKelvey. We recognize that the concepts of paramarginal and submarginal resources are valid, but because of the broader objectives of this volume, nearly all our authors found that a single degree of distinction based on economic recoverability was difficult enough to obtain for identified resources, let alone for undiscovered resources, without the further complication of another degree defined by a specific price factor. Thus, nearly all the chapters of this volume differentiate three major categories of resources—identified, hypothetical, and speculative; within the first category, most chapters differentiate between recoverable identified resources (reserves), and subeconomic identified resources (conditional resources). In only a few chapters have the authors attempted to extend the levels of economic recoverability into the hypothetical and speculative fields, and where this has been done, it is generally in terms of "recoverable" versus "subeconomic"—for example, "subeconomic hypothetical resources."

Special problems are posed in classifying the resources found in sea-floor manganese nodules, in metal-bearing muds of the Red Sea, and in the recently discovered metal-bearing sedimentary rocks of the Belt Supergroup in Idaho and Montana. Some authors were reluctant to characterize the deposits in these three environments as identified resources. We see no question that they are identified, in that they broadly fit the criteria of being known as to existence and location; but we well realize that they are not fully evaluated. Our decision to classify these resources as "identified," for consistency of treatment within this volume, may therefore be regarded as arbitrary and is in no way binding on our authors or on our readers. We note, however, that officials of two major U.S. mining companies were recently reported to have said they "expect to be selling metal made from the [sea-floor] nodules by the end of the decade" (Faltermayer, 1972, p. 170). Such expectations, in our view, are not likely to have been predicated on resources that are undiscovered.

PUBLIC AWARENESS, RESOURCE ESTIMATES, AND GEOLOGIC AVAILABILITY

Public awareness of our dependence on mineral resources appears to be growing. With this growth in awareness—and indeed responsible for some of it—is a growth in the number of magazine and newspaper articles, and even books, that attempt to evaluate our supply of mineral resources and in some cases to forecast economic or cultural trends that are dependent on this supply. (See, for example, Faltermayer, 1972; Meadows and others, 1972; U.S. News and World Report, 1972.) The almost universal tendency of such articles is to discuss mineral resources principally from the perspective of economic availability under a given set of conditions, thereby overlooking the vital fact that reserves are but a part of resources. The results are, we feel, disturbing. Evaluations predicated only on knowledge (or estimates) of current reserves can easily lead to forecasts of the death of the industrial society in a short time. On the other hand, evaluations based on another kind of assumption suggest that a rise in prices will increase the reserves and bring much more material to market economically from lower and lower grade material in larger and larger deposits. This reasoning too is fallacious because elements are available in the earth's crust in very finite amounts. But in both instances, the reasoning leads to serious misinterpretations because it does not give adequate consideration to the single factor that ultimately determines all levels and degrees of mineral potential: *geologic availability*. Geologic availability concerns the existence and concentration of certain elements or combinations of elements and is the most fundamental characteristic of a mineral commodity that governs its commercial use.

Assessment of geologic availability of a commodity requires basic knowledge of the geology, mineralogy, and geochemistry of that material, the geologic environments in which it occurs, and its concentration in those environments. The technology of exploration, mining, beneficiation, recov-

ery, and use is founded upon this information. Studies of geologic availability are indispensable—at all levels of commerce, industry, and government—for any economic planning that considers the available supply or use of primary mineral commodities and their byproducts.

Generally, however, public concepts of the magnitude of mineral resources are based on evaluations of economic rather than geologic availability, and even these are subject to numerous problems. Sound, accurate estimates of reserves for large regions are highly difficult to compile, for many reasons. Reserve data from industrial deposits may not be available because of the problems of competition and taxes. Managements of many companies believe that in the competitive atmosphere of business they should not release information about their reserves. Some States tax the reserves in the ground held by mining companies, making it economically advantageous, and in some cases necessary, to produce at capacity for years from deposits that are continually reported to be nearly exhausted. Definition of tonnages of mineral resources of sufficiently high grade to be minable at current prices is difficult enough without trying to distinguish grades minable at 1.5 or more times greater than the current price. Economic evaluations of a specific mineral deposit have become a complex task for a team of specialists, including not only geologists but also mining engineers, ore dressers, metallurgists, and economists. So many complex factors govern price at any given time that it would seem foolhardy to estimate resources in each of the economic categories and expect the results to be meaningful for very long.

At some time, however, the pressures of both economic and geologic factors will meet in crisis. Economic factors may be altered rapidly. Changes in demand and use alter patterns of production and consumption; new deposits are sought elsewhere; substitutes will be sought; and new technology will be developed as the ingenuity of man is focused on solving the problems. But there is no economic availability if there is no geologic availability. Of the two factors, geologic availability is the more fundamental because without it economic availability is not pertinent. Just as no biological miracle can make it possible to extract blood from a turnip, neither technological magic nor astronomic dollar value can make it possible to extract gold or aluminum or borax or mica from rocks in which they are not present. *Geologic availability, therefore, is the ultimate determinant of mineral potential,* and it is geologic availability that is stressed in the evaluations of potential mineral resources in this volume. Few chapters in the volume attempt to distinguish between tonnages now recoverable and those available only at subeconomic levels of the three "certainty-of-existence" categories shown in figure 1, but virtually every chapter offers a quantitative evaluation in numbers or words for the resources in each of the three categories, and the use of the threefold terminology has been applied as rigorously and uniformly as practical in each chapter.

GENERAL CONCLUSIONS

We realize that this book lacks a plot sufficient to induce its readers into proceeding through it from cover to cover. Therefore, we offer here some general conclusions on several aspects of the Nation's mineral-resource position, which have emerged from our editorial overview of the chapters as a whole. Of first importance is a summary answer to the principal question to which the volume is directed: Where do we stand with regard to resources of each commodity? Other conclusions pertain to the increasing importance, as resources, of large volumes of low-grade rocks, and attendant environmental problems; the problem of enormous quantities of potential mineral byproducts that are now literally being wasted; the factor of energy in the extraction of minerals; and finally, the pressing need for vigorous research along many lines.

MINERAL POTENTIAL: WHERE DO WE STAND?

Each chapter of the volume has its own calculation or other evaluation of resources governed by those factors deemed by the authors to be important to the respective commodity. There is no way to make the data in each chapter absolutely comparable. We would prefer that users of the volume read the chapters of interest to them in order to obtain the best possible understanding of the authors' presentation of resource data, and then formulate their own conclusions. We have, however, compiled a table that shows resource appraisals on a numerical scale, for commodities of major importance, put into perspective in terms of the *minimum* anticipated cumulative demand [1] for the period 1968–2000 as compiled by the U.S. Bureau of Mines (1970). Once again we emphasize that the resources indicated here are for the most part *potential,* and that their eventual availability as reserves is entirely dependent on continued geologic and technologic research as well as economic factors.

[1] In using "demand" values for purposes of comparison we do not represent them as being specific goals to be reached. This volume presents no social or political judgments; its sole purpose is to make available reliable geologic resource facts and assessments for public policy decision as well as for use by the minerals industry.

TABLE 1.—*Potential U.S. resources of some important mineral commodities, in relation to minimum anticipated cumulative demand to year 2000 A.D.*

ST=short tons. lb=pounds.
LT=long tons. Tr oz=troy ounces.
Identified resources: Includes reserves, and materials other than reserves that are reasonably well known as to location, extent, and grade, that may be exploitable in the future under more favorable economic conditions or with improvements in technology.
Hypothetical resources: Undiscovered but geologically predictable deposits of materials similar to present identified resources.
I. Domestic resources (of the category shown) are greater than 10 times the minimum anticipated cumulative demand 1968–2000.
II. Domestic resources are 2 to 10 times the MACD.
III. Domestic resources are approximately 75 percent to 2 times the MACD.
IV. Domestic resources are approximately 35–75 percent the MACD.
V. Domestic resources are approximately 10–35 percent the MACD.
VI. Domestic resources are less than 10 percent of the MACD.

Commodity	Minimum anticipated cumulative demand, 1968–2000 [1]	Identified resources	Hypothetical resources
Aluminum	290,000,000 ST	II	Not estimated.
Asbestos	32,700,000 ST	V	VI
Barite	25,300,000 ST	II	II
Chromium	20,100,000 ST	VI	VI
Clay	2,813,500,000 ST	III	II
Copper	96,400,000 ST	III	III
Fluorine	37,600,000 ST	V	V
Gold	372,000,000 Tr oz	III	Not estimated.
Gypsum	719,800,000 ST	I	I
Iron	3,280,000,000 ST	II	I
Lead	37,000,000 ST	III	IV
Manganese	47,000,000 ST	III	Not estimated.
Mercury	2,600,000 flasks	V	Not estimated.
Mica, scrap	6,000,000 ST	II	I
Molybdenum	3,100,000,000 lbs	I	I
Nickel	16,200,000,000 lbs	III	Not estimated.
Phosphate	190,000,000 ST	II	I
Sand and gravel	56,800,000,000 ST	III	Not estimated.
Silver	3,700,000,000 Tr oz	III	III
Sulfur	473,000,000 LT	I	I
Thorium	27,500 ST [2]	II	Not estimated.
Titanium (TiO_2)	38,000,000 ST	II	II
Tungsten	1,100,000,000 lbs	IV	IV
Uranium	1,190,000 ST	II	III
Vanadium	420,000 ST	II	Not estimated.
Zinc	57,000,000 ST	II	II

[1] As estimated by U.S. Bureau of Mines, 1970.

[2] For thorium, *maximum* anticipated cumulative demand 1968-2000, which assumes commercial development of economically attractive thorium reactors by 1980.

Careful study of both this table and the volume in its entirety leads to the conclusion that only a few commodities are readily available to the United States in quantities adequate to last for hundreds of years. By no means is it too early to become concerned about future mineral supplies—and to start planning. Charles F. Park (1968) wrote of the decrease in mineral supplies that is placing modern American affluence in jeopardy. The real extent of our dependence on mineral resources places in jeopardy not merely affluence, but world civilization.

LOW-GRADE ORES AND THE ENVIRONMENT

The impelling need for minerals poses environmental problems of concern to all. Probably foremost among these is the fact that for many minerals future production will depend on mining enormous volumes of low-grade ores, with necessarily strong environmental impact. The problem can be temporary, and can be solved, as witness the utilization of the manganese deposits in the Nikopol region, U.S.S.R., described in the chapter on "Manganese." But in most areas the opposing factions of industry and environmentalist are still just facing off. We believe the problem must be met squarely, realistically, and soon, by frank and objective exchange—not merely between small groups representing the mining industry on the one hand and outdoor enthusiasts on the other but between industry and the public at large. The environment is far bigger then any small interest group. Ultimately, a concerned public must decide in which order to place its priorities, and each faction of that public is entitled to basic information on the need for and availability of mineral resources as a foundation on which to base its decisions. Thus, as only two examples of such factions, the enthusiastic hiker—whether fisherman, Scout leader, or vacationing city dweller—must realize that his dacron-covered aluminum-frame backpack, his nylon fishing line, his polyurethane foam pad, and even his dehydrated foods are either made of or processed by mineral products, which continue to be used up and must continue to be made available. Conversely, the miner must realize that his assertion of need to develop a new copper deposit, when the technology of extraction may leave not only important potential byproducts but half the copper itself in the ground, may sound more like expediency than need.

It is beyond the scope of this volume to attempt a comprehensive review or evaluation of the mineral-environmental problem in general. Our purpose here is simply to indicate that the chapters of this volume provide some of the basic information on which such reviews or evaluations should be based.

ECONOMICS AND WASTE

A major aspect of resources that appears in many of these chapters is the extent to which many potential byproducts or coproducts are literally being *wasted*—lost forever—because there is no apparent economic incentive for recovering them. Some minerals go into slurry ponds, some into slags, some up the flue. Examples of such commodities are the vanadium in magnetite deposits; selenium, tellurium, and gold lost through in-place leaching of porphyry copper deposits; fluorine, vanadium, uranium, scandium, and rare earths in marine phosphorites; cadmium, bismuth, and cobalt in lead ores; and several metals in coal ash. Strictly speak-

ing, these resources belong in the category of conditional resources, but we believe there is a significant distinction between resources that are not economically minable under present conditions and those that either are not recovered because of selective mining, or are discarded because of selective processing. In many cases the perspective of geologic availability makes possible the view that what may seem economical for the short term is not necessarily so for the long term, and these potential resources should not be overlooked or misused.

THE ENERGY FACTOR

Extraction and processing of all minerals requires some form of energy, and it is a safe generalization to say that to produce a fixed amount of any given commodity, the lower the grade of ore, the greater is the quantity of energy required. Although this volume contains individual chapters on mineral energy resources, a comprehensive evaluation of energy resources in the context of their specific relation to extraction of minerals is far beyond the scope of the book. The reader should bear in mind that as the mining industry turns to lower and lower grades of many ores, the cost and availability of the required energy are probably the single most important factors that will ultimately determine whether or not a particular mineral deposit can be worked economically.

THE NEED FOR RESEARCH

Potential resources are transformed into reserves not by moving rock, but by expanding the artificial boundaries of geologic knowledge and economic availability that delimit "reserves" from "resources"; hence, the potential of most of the resources discussed in this volume can be realized only as a result of applied research. Development of new technologies will make economic extraction of conditional resources feasible; innovative application of old geologic theory and the creation of new concepts of ore formation can be expected to lead to the discovery of conventional mineral deposits in favorable regions (hypothetical resources); research and exploration can be counted on to discover some new types of deposits and some new ore environments and regions that we do not know about now (speculative resources).

Clearly, to these factors of geologic and economic availability we must also add the factor of human ingenuity. W. E. Pratt (1943), vice president of Standard Oil Co., in speaking some years ago of petroleum exploration, cogently expressed a viewpoint that is equally pertinent for mineral exploration: "* * * physical conditions in the earth's crust impose fewer and less formidable obstacles to the development of commercial oil fields over the earth than do some of our mental and social habits * * * . Whatever the geological conditions may be and whatever technique we employ, we find oil in the earth very rarely unless we have first acquired an appropriate mental attitude * * *. Where oil really is, then, in the final analysis, is in our own heads!"

The chapters of this volume constitute a beginning effort to cultivate the "appropriate mental attitude" and to articulate the resulting ideas in terms of where and in what magnitudes our future mineral resources might be found. Only by continuing this effort, through vigorous pursuit of exploration, research, and technologic development, can we confidently expect to locate these potential resources and convert them into usable reserves.

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MINERAL RESOURCE ESTIMATES AND PUBLIC POLICY

By V. E. McKelvey

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INTRODUCTION

Not many people, I have found, realize the extent of our dependence on minerals. It was both a surprise and a pleasure, therefore, to come across the observations of George Orwell in his book "The Road to Wigan Pier." When describing the working conditions of English miners in the 1930's, he evidently was led to reflect on the significance of coal:

> Our civilization . . . is founded on coal, more completely than one realizes until one stops to think about it. The machines that keep us alive, and the machines that make the machines are all directly or indirectly dependent upon coal . . . . Practically everything we do, from eating an ice to crossing the Atlantic, and from baking a loaf to writing a novel, involves the use of coal, directly or indirectly. For all the arts of peace coal is needed; if war breaks out it is needed all the more. In time of revolution the miner must go on working or the revolution must stop, for revolution as much as reaction needs coal . . . In order that Hitler may march the goosestep, that the Pope may denounce Bolshevism, that the cricket crowds may assemble at Lords, that the Nancy poets may scratch one another's backs, coal has got to be forthcoming.

To make Orwell's statement entirely accurate—and ruin its force with complications—we should speak of mineral *fuels*, instead of coal, and of other minerals also, for it is true that minerals and mineral fuels are the resources that make the industrial society possible. The essential role of minerals and mineral fuels in human life may be illustrated by a simple equation

$$L=\frac{R\times E\times I}{P}$$

in which the society's average level of living (L), measured in its useful consumption of goods and services, is seen to be a function of its useful consumption of all kinds of raw materials (R), including metals, nonmetals, water, soil minerals, biologic produce, and so on; times its useful consumption of all forms of energy (E); times its useful consumption of all forms of ingenuity (I), including political and socio-economic as well as technologic ingenuity; divided by the number of people (P) who share in the total product.

This is a restatement of the classical economists' equation in which national output is considered to be a function of its use of capital and labor, but it shows what capital and labor really are. Far from being mere money, which is what it is popularly thought to mean, capital represents accumulated usable raw materials and things made from them, usable energy, and especially accumulated knowl-

edge. And the muscle power expended in mere physical toil, which is what labor is often thought to mean, is a trivial contribution to national output compared to that supplied by people in the form of skills and ingenuity.

This is only a conceptual equation, of course, for numerical values cannot be assigned to some of its components, and no doubt some of them—ingenuity in particular—should receive far more weight than others. Moreover, its components are highly interrelated and interdependent. It is the development and use of a high degree of ingenuity that makes possible the high consumption of minerals and fuels, and the use of minerals and fuels are each essential to the availability and use of the other. Nevertheless, the expression serves to emphasize that level of living is a function of our intelligent use of natural resources, and it brings out the importance of the use of energy and minerals in the industrial society. As shown in figure 2, per capital Gross National Product among the countries of the world is, in fact, closely related to their per capita consumption of energy. Steel consumption also shows a close relation to per capita GNP (fig. 3), as does the consumption of many other minerals.

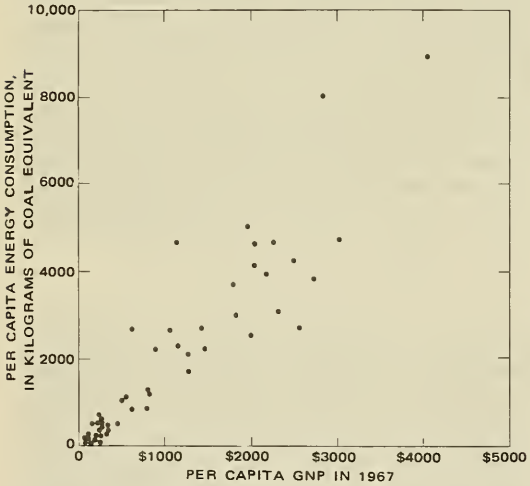

FIGURE 2.—Per capita energy consumption compared to per capita Gross National Product (GNP) in countries for which statistics are available in the United Nations "Statistical Yearbook" for 1967.

Because of the key role that minerals and fuels play in economic growth and in economic and military security, the extent of their resources is a matter of great importance to government, and questions concerning the magnitude of resources arise in conjunction with many public problems. To cite some recent examples, the magnitude of low-cost coal and uranium reserves has been at the heart of the question as to when to press the development of the breeder reactor—which requires a research-and-development program involving such an enormous outlay of public capital that it would be unwise to make the investment until absolutely necessary.

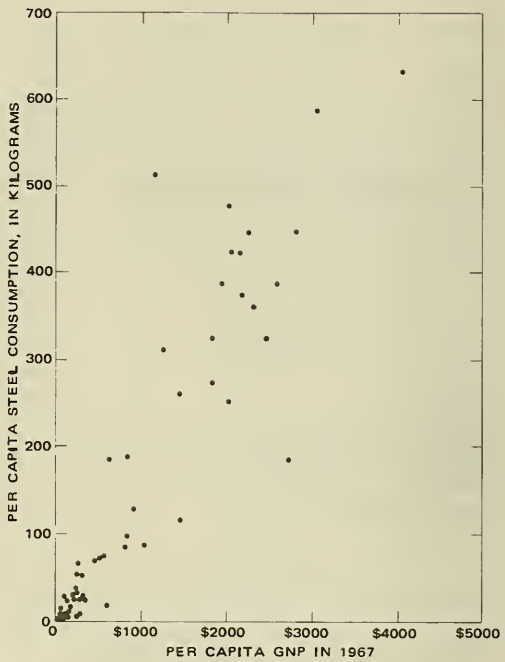

FIGURE 3.—Per capita steel consumption compared to per capita Gross National Product (GNP) in countries for which statistics are available in the United Nations "Statistical Yearbook" for 1967.

Similarly, estimates of potential oil and gas resources are needed for policy decisions related to the development of oil shale and coal as commercial sources of hydrocarbons, and estimates are needed also as the basis for decisions concerning prices and import controls.

Faced with a developing shortage of natural gas, the Federal Power Commission is presently much interested in knowing whether or not reserves reported by industry are an accurate indication of the

amount of natural gas actually on hand; it also wants to know the extent of potential resources and the effect of price on their exploration and development. At the regional or local level, decisions with respect to the designation of wilderness areas and parks, the construction of dams, and other matters related to land use involve appraisal of the distribution and amount of the resources in the area. The questions of the need for an international regime governing the development of seabed resources, the character such arrangement should have, the definition of the area to which it should apply also involve, among other considerations, analysis of the probable character, distribtuion, and magnitude of subsea mineral resources.

And coming to the forefront is the most serious question of all—namely, whether or not resources are adequate to support the continued existence of the world's population and indeed our own. The possibility to consider here goes much beyond Malthus' gloomy observations concerning the propensity of a population to grow to the limit of its food supply, for both population and level of living have grown as the result of the consumption of nonrenewable resources, and both are already far too high to maintain without industrialized, high-energy, and high mineral-consuming agriculture, transportation, and manufacturing. I will say more about this question later, but to indicate something of the magnitude of the problem let me point out that, in attaining our high level of living in the United States, we have used more minerals and mineral fuels during the last 30 years than all the people of the world used previously. This enormous consumption will have to be doubled just to meet the needs of the people now living in the United States through the remainder of their lifetimes, to say nothing about the needs of succeeding generations, or the increased consumption that will have to take place in the lesser developed countries if they are to attain a similar level of living.

CONCEPTS OF RESERVES AND RESOURCES

The focus of most of industry's concern over the extent of mineral resources is on the magnitude of the supplies that exist now or that can be developed in the near term, and this is of public interest also. Many other policy decisions, however, relate to the much more difficult question of potential supplies, a question that to be answered properly must take account both of the extent of undiscovered deposits as well as deposits that cannot be produced profitably now but may become workable in the future. Unfortunately, the need to take account of such deposits is often overlooked, and there is a widespread tendency to think of potential resources as consisting merely of materials in known deposits producible under present economic and technologic conditions.

In connection with my own involvement in resource appraisal, I have been developing over the last several years a system of resource classification and terminology that brings out the classes of resources that need to be taken into account in appraising future supplies, which I believe helps to put the supply problem into a useful perspective. Before describing it, however, I want to emphasize that the problem of estimating potential resources has several built-in uncertainties that make an accurate and complete resource inventory impossible, no matter how comprehensive its scope.

One such uncertainty results from the nature of the occurrence of mineral deposits, for most of them lie hidden beneath the earth's surface and are difficult to locate and to examine in a way that yields accurate knowledge of their extent and quality. Another source of uncertainty is that the specifications of recoverable materials are constantly changing as the advance of technology permits us to mine or process minerals that were once too low in grade, too inaccessible, or too refractory to recovery profitably. Still another results from advances that make it possible to utilize materials not previously visualized as usable at all.

For these reasons the quantity of usable resources is not fixed but changes with progress in science, technology, and exploration and with shifts in economic conditions. We must expect to revise our estimates periodically to take account of new developments. Even incomplete and provisional estimates are better than none at all, and if they differentiate known, undiscovered, and presently uneconomic resources they will help to define the supply problem and provide a basis for policy decisions relating to it.

The need to differentiate the known and the recoverable from the undiscovered and the uneconomic requires that a resource classification system convey two prime elements of information: the degree of certainty about the existence of the materials and the economic feasibility of recovering them. These two elements have been recognized in existing terminology, but only incompletely. Thus as used by both the mining and the petroleum industries, the term reserves generally refers to economically recoverable material in identified deposits, and the term resources includes in addition deposits not yet discovered as well as identified deposits that

cannot be recovered now (for example, Blondel and Lasky, 1956).

The degree of certainty about the existence of the materials is described by terms such as **proved, probable,** and **possible,** the terms traditionally used by industry, and **measured, indicated,** and **inferred,** the terms devised during World War II by the Geological Survey and the Bureau of Mines to serve better the broader purpose of national resource appraisal. Usage of these degree-of-certainty terms is by no means standard, but all their definitions show that they refer only to deposits or structures known to exist.

Thus, one of the generally accepted definitions of **possible** ore states that it is to apply to deposits whose existence is known from at least one exposure, and another definition refers to an ore body sampled only on one side. The definition of **inferred** reserves agreed to by the Survey and the Bureau of Mines permits inclusion of completely concealed deposits for which there is specific geologic evidence and for which the specific location can be described, but it makes no allowance for ore in unknown structures of undiscovered districts. The previous definitions of both sets of terms also link them to deposits minable at a profit; the classification system comprised of these terms has thus neglected deposits that might become minable as the result of technologic or economic developments.

To remedy these defects, I have suggested that existing terminology be expanded into the broader framework shown in figure 4, in which degree of certainty increases from right to left and feasibility of economic recovery increases from bottom to top. Either of the series of terms already used to describe degree of certainty may be used with reference to identified deposits and applied not only to presently minable deposits but to others that have been identified with the same degree of certainty. Feasibility-of-recovery categories are designated by the terms **recoverable, paramarginal,** and **submarginal.**

Paramarginal resources are defined here as those that are recoverable at prices as much as 1.5 times those prevailing now. (I am indebted to S. P. Schweinfurth for suggesting the prefix para to indicate that the materials described are not only those just on the margin of economic recoverability, the common economic meaning of the term **marginal.**) At first thought this price factor may seem to be unrealistic. The fact is, however, that prices of many mineral commodities vary within such a range from place to place at any given time, and a price elas-

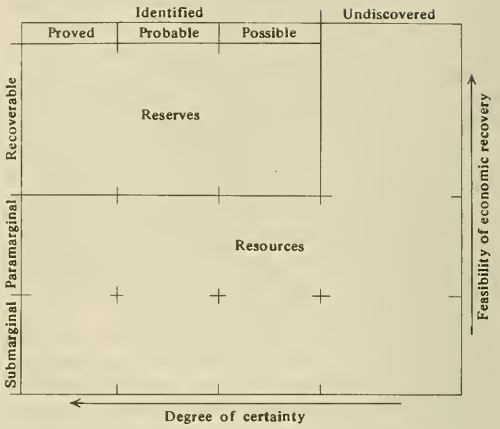

FIGURE 4.—Classification of mineral reserves and resources. Degree of certainty increases from right to left, and feasibility of economic recovery increases from bottom to top.

ticity of this order of magnitude is not uncommon for many commodities over a space of a few years or even months, as shown by recent variations in prices of copper, mercury, silver, sulfur, and coal. Deposits in this category thus become commercially available at price increases that can be borne without serious economic effects, and chances are that improvements in existing technology will make them available at prices little or no higher than those prevailing now.

Over the longer period, we can expect that technologic advances will make it profitable to mine resources that would be much too costly to produce now, and, of course, that is the reason for trying to take account of submarginal resources. Again, it might seem ridiculous to consider resources that cost two or three times more than those produced now as having any future value at all. But keep in mind, as one of many examples, that the cutoff grade for copper has been reduced progressively not just by a factor of two or three but by a factor of 10 since the turn of the century and by a factor of about 250 over the history of mining. Many of the fuels and minerals being produced today would once have been classed as submarginal under this definition, and it is reasonable to believe that continued technologic progress will create recoverable reserves from this category.

EXAMPLES OF ESTIMATES OF POTENTIAL RESOURCES

For most minerals, the chief value of this classification at present is to call attention to the information needed for a comprehensive appraisal of their potential, for we haven't developed the knowledge and the methods necessary to make meaningful estimates of the magnitude of undiscovered deposits, and we don't know enough about the cost of producing most presently noncommercial deposits to separate paramarginal from submarginal resources. Enough information is available for the mineral fuels, however, to see their potential in such a framework.

The fuel for which the most complete information is available is the newest one—uranium. As a result of extensive research sponsored by the Atomic Energy Commission, uranium reserves and resources are reported in several cost-of-recovery categories, from less than $8 to more than $100 per pound of U_3O_8. For the lower cost ores, the AEC makes periodic estimates in two degree-of-certainty categories, one that it calls reasonably assured reserves and the other it calls additional resources, defined as uranium surmised to occur in unexplored extensions of known deposits or in undiscovered deposits in known uranium districts. Both the AEC and the Geological Survey have made estimates from time to time of resources in other degree-of-certainty and cost-of-recovery categories.

Ore in the less-than-$8-per-pound class is minable now, and the AEC estimates reasonably assured reserves to be 143,000 tons and additional resources to be 167,000 tons of U_3O_8—just about enough to supply the lifetime needs of reactors in use or ordered in 1968 and only half that required for reactors expected to be in use by 1980. The Geological Survey, however, estimates that undiscovered resources of presently minable quality may amount to 750,000 tons, or about 2.5 times that in identified deposits and districts. Resources in the $8- to $30-a-pound category in identified and undiscovered deposits add only about 600,000 tons of U_3O_8 and thus do not significantly increase potential reserves.

But tens of millions of tons come into prospect in the price range of $30 to $100 per pound. Uranium at such prices would be usable in the breeder reactor. The breeder, of course, would utilize not only U^{235} but also U^{238}, which is 140 times more abundant than U^{235}. Plainly the significance of uranium as a commercial fuel lies in its use in the breeder reactor, and one may question, as a number of critics have (for example, Inglis, 1971), the advisability of enlarging nuclear generating capacity until the breeder is ready for commercial use.

Until recently the only information available about petroleum resources consisted of estimates of proved reserves prepared annually by the American Petroleum Institute and the American Gas Association, plus a few estimates of what has been called ultimate production, that is, the total likely to be eventually recovered. A few years ago, however, the API began to report estimates of total oil in place in proved acreage, and the Potential Gas Committee began to estimate possible and probable reserves of natural gas, defining them as consisting of gas expected to be found in extensions of identified fields and in new discoveries in presently productive strata in producing provinces. It also introduced another category, speculative resources—equivalent to what I have called "undiscovered"—to represent gas to be found in nonproducing provinces and in presently unproductive strata in producing provinces.

In 1970 the National Petroleum Council released a summary of a report on "Future Petroleum Provinces of the United States," prepared at the request of the Department of the Interior, in which it reported estimates of crude oil in the combined probable-possible class and in the speculative category. In addition, NPC estimated the amounts that would be available under two assumptions as to the percent of the oil originally in place that might be recovered in the future (table 2). NPC did not assess the cost of such recovery, but the average recovery is now about 30 percent of the oil in place, and NPC expects it to increase gradually to about 42 percent in the year 2000 and to 60 percent eventually. The NPC estimates do not cover all potentially favorable areas either on land or offshore but, even so, in the sum of these various categories NPC sees about 12 times as much oil remaining to be discovered and produced as exists in proved reserves alone.

The Potential Gas Committee's estimates of potential gas resources similarly do not cover all favorable areas, but they indicate that resources in the probable, possible, and speculative categories are about twice that of proved reserves and past production. Because about 80 percent of the gas originally in place is now recovered, paramarginal and submarginal resources in ordinary gas reservoirs are not as large as for crude oil. Paramarginal and submarginal gas resources may be significant, however, in kinds of rocks from which gas is not now recovered, namely impermeable strata and coal. In the Rocky Mountain province, for instance, Haun, Barlow, and Hallinger (1970) recently estimated

TABLE 2.—*Some estimates of U.S. crude-oil reserves and resources, in billion barrels*

[API, American Petroleum Institute; NPC, National Petroleum Council]

	In identified fields or stuctures		In undiscovered fields and structures (speculative)
	Proved	Probable-possible	
Recoverable at present rate [1]	31 (API)	74 (NPC)	67 (NPC)
Additional at 42 percent recovery	47 (NPC)	22 (NPC)	21 (NPC)
Additional at 60 percent recovery	69 (NPC)	40 (NPC)	37 (NPC)
Oil originally in place	388 (API) [2]	227 (NPC)	209 (NPC)
Total oil originally in place	2200 (Hendricks and Schweinfurth, 1968).		
Ultimate production [2]	190 (Hubbert, 1969); 353 (Moore, 1966); 433 (Weeks) [3]; 450 (Elliott and Linden, 1968); 432–495 (NPC); 550 (Hendricks and Schweinfurth, 1968).		

[1] Average recovery is 30 percent of oil in place.
[2] Includes past production of 86 billion barrels.
[3] See McKelvey (1968, Table II, p. 18).

potential gas resources in ordinary reservoirs to be in the range of 100 to 200 trillion cubic feet, but pointed out that gas in impermeable strata which might be released by nuclear stimulation would be several times that amount. Gas occluded in coal—now only a menace in this country as a cause of explosions—is already recovered in some European mines and is also a potentially large resource.

The uncertainties concerning potential coal resources center not on their total magnitude, as they do for oil and gas, but on the amounts available at present prices. Because coal beds have great lateral continuity, geologic mapping and stratigraphic studies make it possible to project them long distances from their outcrops and to categorize them in terms of thickness of beds, thickness of overburden, rank of coal, and other features that affect cost. The Geological Survey has prepared such estimates, but the cost of recovering coal in the various categories has yet to be determined. Coal in beds more than 14 inches thick totals at least 3.3 trillion tons in the United States, but estimates of the amounts minable at present prices have ranged from 20 to 220 billion tons. (See U.S. Office of Science and Technology, "Energy R and D and National Progress.") Because 20 billion tons represents nearly a 40-year supply at present rates of consumption, it is easy to see why the studies needed to determine how much would be available at various costs have not been undertaken. The question is by no means only of academic interest, for the nuclear power development program was justified in part in its early years on the assumption that reserves of low-cost coal were extremely limited, and part of the continued growth of the nuclear power industry is said to be the result of the difficulty power companies are having in acquiring low-cost reserves.

QUANTIFYING THE UNDISCOVERED

Considering potential resources in the degree-of-certainty, cost-of-recovery framework brings out the joint role that geologists, engineers, mineral technologists, and economists must play in estimating their magnitude. Having emphasized the importance of the economic and technologic side of the problem, I want now to turn to the geological side and consider the problem of how to appraise the extent of undiscovered reserves and resources.

It is difficult enough to estimate the extent of unexplored resources of the inferred or possible class. In fact, it is even difficult to estimate measured or proved reserves with a high degree of accuracy until they have been largely mined out. Thus, estimates of proved reserves prepared in advance of appreciable production commonly have an error of about 25 percent, and the error in estimates of incompletely explored deposits is usually much larger. Generally the combination of the geologist's inherent conservatism and the lack of information on the geology of concealed areas leads to estimates that err in being too low rather than too high.

One eminent mining geologist reported that, having recognized these effects, he once arbitrarily tripled his calculations to arrive at an estimate of the ore remaining in a producing district; twice the amount of his inflated estimate, however, was found and mined over the next 20 years, and more was in prospect. To match many such stories are at least a few prematurely deserted mills and mine installations built on the expectation of finding ore that did not materialize. Both kinds of experiences emphasize the difficulty of appraising the extent of mineral deposits even in partly explored areas. In the light of such experiences one is justified in asking—as many well-informed people have—whether estimates of the magnitude of undiscovered deposits can have enough reliability to make them worthwhile.

The fact that new districts are still being discovered for nearly every commodity and that large areas favorable for the occurrence of minerals of all kinds are covered by alluvium, volcanics, glacial

drift, seawater, or other materials that conceal possible mineral-bearing rocks or structures assures us that undiscovered deposits are still to be found. Qualitatively, at least, we know something about the distribution of minerals with respect to other geologic phenomena and, if this is so, we have a chance of developing quantitative relations that will give us at least a start.

Two principal approaches to the problem have been taken thus far. One is to extrapolate observations related to rate of industrial activity, such as annual production of the commodity; the other is to extrapolate observations that relate to the abundance of the mineral in the geologic environment in which it is found.

The first of these methods has been utilized by M. K. Hubbert (1969), C. L. Moore (1966), and M. A. Elliott and H. R. Linden (1968) in estimating ultimate reserves of petroleum. The essential features of this approach are to analyze the growth in production, proved reserves, and discovery per foot of drilling over time and to project these rate phenomena to terminal values in order to predict ultimate production. Hubbert has used the logistic curve for his projections, and Moore has utilized the Gompertz curve, with results more than twice as high as those of Hubbert. As Hubbert has pointed out, these methods utilize the most reliable information collected on the petroleum industry; modern records on production, proved reserves, number of wells drilled, and similar activities are both relatively complete and accurate, at least as compared with quantitative knowledge about geologic features that affect the distribution of petroleum.

The rate methods, however, have an inherent weakness in that the phenomena they analyze reflect human activities that are strongly influenced by economic, political, and other factors that bear no relation to the amount of oil or other material that lies in the ground. Moreover, they make no allowance for major breakthroughs that might transform extensive paramarginal or submarginal resources into recoverable reserves, nor do they provide a means of estimating the potential resources of unexplored regions. Such projections have some value in indicating what will happen over the short term if recent trends continue, but they can have only limited success in appraising potential resources.

Even the goal of such projections, namely the prediction of ultimate production, is not a useful one. Not only is it impossible to predict the quantitative effects of man's future activities but the concept implies that the activities of the past are a part of an inexorable process with only one possible outcome. Far more useful, in my opinion, are estimates of the amounts of various kinds of materials that are in the ground in various environments; such estimates establish targets for both the explorer and the technologist, and they give us a basis for choosing among alternative ways of meeting our needs for mineral supplies.

The second principal approach taken thus far to the estimation of undiscovered resources involves the extrapolation of data on the abundance of mineral deposits from explored to unexplored ground on the basis of either the area or the volume of broadly favorable rocks. In the field of metalliferous deposits, Nolan (1950) pioneered in extrapolation on the basis of area in his study of the spatial and size distribution of mineral deposits in the Boulder Dam region and in his conclusion that a similar distribution should prevail in adjacent concealed and unexplored areas. Weeks (1958, 1965) and Pratt (1950) played similar roles with respect to the estimation of petroleum resources—Weeks extrapolating on the basis of oil per unit volume of sediment and Pratt on the basis of oil per unit area. Many of the estimates of crude oil that went into the NPC study were made by the volumetric method, utilizing locally appropriate factors on the amount of oil expected per cubic mile of sediment. Olson and Overstreet (1964) have since used the area method to estimate the magnitude of world thorium resources as a function of the size of areas of igneous and metamorphic rocks as compared with India and the United States, and A. P. Butler (written commun., 1958) used the magnitude of sandstone uranium ore reserves exposed in outcrop as a basis for estimating the area in back of the outcrop that is similarly mineralized.

Several years ago, Zapp (1962) and Hendricks (1965) introduced another approach, based on the amount of drilling required to explore adequately the ground favorable for exploration and the reserves discovered by the footage already drilled—a procedure usable in combination with either the volumetric or areal approach. Recently J. B. Zimmerman and F. L. Long (cited in "Oil and Gas Journal, 1969") applied this approach to the estimation of gas resources in the Delaware–Val Verde basins of west Texas and southeastern New Mexico; and Haun, Barlow, and Hallinger (1970) used it to estimate potential natural gas resources in the Rocky Mountain region. In the field of metals, Lowell (1970) has estimated the number of undiscovered porphyry copper deposits in the southwestern United States, Chile and Peru, and British Columbia as a function of the proportion of the

favorable pre-ore surface adequately explored by drilling, and Armstrong (1970) has similarly estimated undiscovered uranium reserves in the Gas Hills area of Wyoming on the basis of the ratios between explored and unexplored favorable areas.

I have suggested another variant of the areal method for estimating reserves of nonfuel minerals which is based on the fact that the tonnage of minable reserves of the well-explored elements in the United States is roughly equal to their crustal abundance in percent times a billion or 10 billion (fig. 5). Obviously this relation is influenced by the

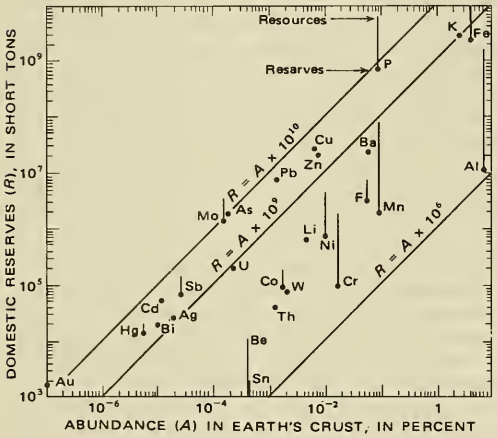

FIGURE 5.—Domestic reserves of elements compared to their abundance in the earth's crust. Tonnage of ore minable now is shown by a dot; tonnage of lowergrade ores whose exploitation depends upon future technological advances or higher prices is shown by a bar.

extent of exploration, for it is only reserves of the long-sought and well-explored minerals that display the relation to abundance. But it is this feature that gives the method its greatest usefulness, for it makes it possible to estimate potential resources of elements, such as uranium and thorium, that have been prospected for only a short period. Sekine (1963) tested this method for Japan and found it applicable there, which surprised me a little, for I would not have thought Japan to be a large enough sample of the continental crust to bring out this relationship.

The relation between reserves and abundance, of course, can at best be only an approximate one, useful mainly in order-of-magnitude estimates, for obviously crustal abundance of an element is only one of its properties that lead to its concentration. That it is an important factor, however, may be seen not only in its influence on the magnitude of reserves but also in other expressions of its influence on the concentrations of the elements. For example, of the 18 or so elements with crustal abundances greater than about 200 parts per million, all but fluorine and strontium are rock forming in the sense that some extensive rocks are composed chiefly of minerals of which each of these elements is a major constituent. Of the less abundant elements, only chromium, nitrogen, and boron have this distinction. Only a few other elements, such as copper, lead, and zinc, even form ore bodies composed mainly of minerals of which the valuable element is a major constituent, and in a general way the grade of minable ores decreases with decreasing crustal abundance. A similar gross correlation exists between abundance of the elements and the number of minerals in which they are a significant constituent.

Members of a committee of the Geology and the Conservation of Mineral Resources Board of the Soviet Union have described a somewhat similar method for the quantitative evaluation of what they call predicted reserves of oil and gas, based on estimates of the total amount of hydrocarbons in the source rock and of the fraction that has migrated into commercial reservoirs—estimates that would be much more difficult to obtain for petroleum than for the elements. Probably for this reason not much use has been made of this method, but it seems likely that quantitative studies of the effects of the natural fractionation of the elements might be of some value in estimating total resources in various size and grade categories.

Some studies of the grade-frequency distribution of the elements have, in fact, been undertaken by geochemists in the last couple of decades, and, taking off from Nolan's work, several investigators have studied the areal and size-frequency distribution of mineral deposits in conjunction with attempts to apply the methods of operations research to exploration (for example, Allais, 1957; Slichter, 1960; Griffiths, 1964; DeGeoffroy and Wu, 1970, and Harris and Euresty, 1969). None of these studies has been concerned with the estimation of undiscovered reserves, but they have identified two features about the distribution of mineral deposits that may be applicable to the problem.

One is that the size distribution of both metalliferous deposits, expressed in dollar value of production, and of oil and gas, expressed in volumetric units, has been found to be log normal, which means

that of a large population of deposits, a few contain most of the ore (for example, Slichter, 1960; Kaufman, 1963). In the Boulder Dam area, for example, 4 percent of the districts produced 80 percent of the total value of recorded production. The petroleum industry in the United States has a rule of thumb that 5 percent of the fields account for 50 percent of the reserves and 50 percent of fields, for 95 percent. And in the USSR, about 5 percent of the oil fields contain about 75 percent of the oil, and 10 percent of the gas fields have 85 percent of the gas reserves.

The other feature of interest is that in many deposits the grade-tonnage distribution is also log normal, and the geochemists have found this to be the case also with the frequency distribution of minor elements.

These patterns of size- and grade-frequency distribution will not in themselves provide information on the magnitude of potential resources, for they describe only how minerals are distributed and not how much is present. But if these patterns are combined with quantitative data on the incidence of congeneric deposits in various kinds of environments, the volume or area of favorable ground, and the extent to which it has been explored, they might yield more useful estimates of potential resources than are obtainable by any of the procedures so far applied. Thus, estimates of total resources described in terms of their size- and grade-frequency distributions could be further analyzed in the light of economic criteria defining the size, grade, and accessibility of deposits workable at various costs, and then partitioned into feasibility-of-recovery and degree-of-certainty categories to provide targets for exploration and technologic development as well as guidance for policy decisions.

Essential for such estimates, of course, is better knowledge than is now in hand for many minerals on the volume of ore per unit of favorable ground and on the characteristics of favorable ground itself. For petroleum the development of such knowledge is already well advanced. For example, whereas most estimates of resources have been based on an assumed average petroleum content of about 50,000 barrels per cubic mile of sediment, varied a little perhaps to reflect judgments of favorability, the range in various basins is from 10,000 to more than 2,000,000 barrels per cubic mile. As shown by the recent analysis by Halbouty and his colleagues (1970) of the factors affecting the formation of giant fields, the geologic criteria are developing that make it possible to classify sedimentary basins in terms of their petroleum potential. Knowledge of the mode of occurrence and genesis of many metalliferous minerals and of the geology of the terranes in which they occur is not sufficient to support comprehensive estimates prepared in this way. But for many kinds of deposits enough is known to utilize this kind of approach on a district or regional basis, and I hope a start can soon be made in this direction.

NEED FOR REVIEW OF RESOURCE ADEQUACY

Let me return now to the question of whether or not resources are adequate to maintain our present level of living. This is not a new question by any means. In 1908 it was raised as a national policy issue at the famous Governors' Conference on Resources, and it has been the subject of rather extensive inquiry by several national and international bodies since then. In spite of some of the dire predictions about the future made by various people in the course of these inquiries, they did not lead to any major change in our full-speed-ahead policy of economic development. Some of these inquirles, in fact, led to immediate investigations that revealed a greater resource potential for certain minerals than had been thought to exist, and the net effect was to alleviate rather than heighten concern.

Now, however, concern about resource adequacy is mounting again. The overall tone of the recent National Academy of Sciences' report on "Resources and Man" was cautionary if not pessimistic about continued expansion in the production and use of mineral resources, and many scientists, including some eminent geologists, have expressed grave doubts about our ability to continue on our present course. The question is also being raised internationally, particularly in developing countries where concern is being expressed that our disproportionate use of minerals to support our high level of living may be depriving them of their own future.

Personally, I am confident that for millennia to come we can continue to develop the mineral supplies needed to maintain a high level of living for those who now enjoy it and raise it for the impoverished people of our own country and the world. My reasons for thinking so are that there is a visible undeveloped potential of substantial proportions in each of the processes by which we create resources and that our experience justifies the belief that these processes have dimensions beyond our knowledge and even beyond our imagination at any given time.

Setting aside the unimaginable, I will mention some examples of the believable. I am sure all geolo-

gists would agree that minable undiscovered deposits remain in explored as well as unexplored areas and that progress in our knowledge of regional geology and in exploration will lead to the discovery of many of them. With respect to unexplored areas, the mineral potential of the continental margins and ocean basins deserves particular emphasis, for the technology that will give us access to it is clearly now in sight. For many critical minerals, we already know of substantial paramarginal and submarginal resources that experience tells us should be brought within economic reach by technological advance. The process of substituting an abundant for a scarce material has also been pursued successfully, thus far not out of need but out of economic opportunity, and plainly has much potential as a means of enlarging usable resources.

Extending our supplies by increasing the efficiency of recovery and use of raw materials has also been significant. For example, a unit weight of today's steel provides 43 percent more structural support than it did only 10 years ago, reducing proportionately the amount required for a given purpose. Similarly, we make as much electric power from 1 ton of coal now as we were able to make from 7 tons around the turn of the century. Our rising awareness of pollution and its effects surely will force us to pay even more attention to increasing the efficiency of mineral recovery and use as a means of reducing the release of contaminants to the environment. For similar reasons, we are likely to pursue more diligently processes of recovery, reuse, and recycling of mineral materials than we have in the past.

Most important to secure our future is an abundant and cheap supply of energy, for if that is available we can obtain materials from low-quality sources, perhaps even country rocks, as Harrison Brown (1954, p. 174–175) has suggested. Again. I am personally optimistic on this matter, with respect to the fossil fuels and particularly to the nuclear fuels. Not only does the breeder reactor appear to be near enough to practical reality to justify the belief that it will permit the use of extremely low-grade sources of uranium and thorium that will carry us far into the future, but during the last couple of years there have been exciting new developments in the prospects for commercial energy from fusion. Gothermal energy has a large unexploited potential, and new concepts are also being developed to permit the commercial use of solar energy.

But many others do not share these views, and it seems likely that soon there will be a demand for a confrontation with the full-speed-ahead philosophy that will have to be answered by a deep review of resource adequacy. I myself think that such a review is necessary, simply because the stakes have become so high. Our own population, to say nothing of the world's, is already too large to exist without industrialized, high energy- and mineral-consuming agriculture, transportation, and manufacturing. If our supply of critical materials is enough to meet our needs for only a few decades, a mere tapering off in the rate of increase of their use, or even a modest cutback, would stretch out these supplies for only a trivial period. If resource adequacy cannot be assured into the far-distant future, a major reorientation of our philosophy, goals, and way of life will be necessary. And if we do need to revert to a low resource-consuming economy, we will have to begin the process as quickly as possible in order to avoid chaos and catastrophe.

Comprehensive resource estimates will be essential for this critical examination of resource adequacy, and they will have to be made by techniques of accepted reliability. The techniques I have described for making such estimates have thus far been applied to only a few minerals, and none of them have been developed to the point of general acceptance. Better methods need to be devised and applied more widely, and I hope that others can be enlisted in the effort necessary to do both.

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CRUSTAL ABUNDANCE OF ELEMENTS, AND MINERAL RESERVES AND RESOURCES

By Ralph L. Erickson

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ABSTRACT OF CONCLUSIONS

Crustal abundance data and the reserve-abundance ($R=A\times10^{9-10}$) relationship of McKelvey are combined to calculate the total amounts of several metals in the earth's crust, in various segments of the crust, in United States crust, in United States crust to a 1-kilometer depth, and in the potential currently recoverable resources. Marginal resources are not reported. The potential recoverable resource for most elements should approach $R=2.45A\times10^6$, where A is abundance expressed in grams per metric ton or parts per million and R is resource expressed in metric tons. Those metals whose known reserves most closely approach the calculated potential recoverable resource are the metals that have been most diligently sought for the longest time (lead, copper, zinc, silver, gold, molybdenum). Those metals whose known reserves are very much less than the calculated potential recoverable resource (nickel, tin) are the metals usually found in geologic environments not common in the United States. Those metals whose reserve-potential resource relation is intermediate between crustal abundance and reserve abundance are those that have not been vital to our economy in the past, whose prices are subject to great fluctuation, or whose past source has been chiefly as a by-product. Thus, the scheme of predicting resource potentials in relation to crustal abundance seems valid—if we search for an element hard enough, we find it in about the quantities we might expect.

If we accept the abundance-reserve relationship, it follows that $R=2.45\times10^6$ is a minimum total resource estimate because the relationship is based upon *currently recoverable* resources and does not include resources whose feasibility of economic recovery is not established. Substantial variations of total resource estimates from this formula probably are caused by geologic factors and the inherent geochemical nature of the element. However, recent discoveries of several *new* types of mineral deposits indicate that we need to critically examine our criteria for where and how to look for mineral deposits. Certainly, significant mineral deposists remain undiscovered because exploration efforts are commonly confined to the classic environments of ore deposition.

ABUNDANCE-RESOURCE-RESERVE RELATIONSHIPS

The table of abundance, reserves, and potential resources of some metals in the earth's crust and United States crust presented in this chapter provides a broad general framework in which to examine the relation between abundance, reserves, and resources. The abundance data used for mass and resource calculations are based upon the work of Lee and Yao (1970). These authors have taken into account oceanic crust, variation with depth of continental crust, and variation between shield areas, folded belts, and volcanic arcs. They also provide reasonable figures for thickness and mass of the various subdivisions of earth's crust.

McKelvey (1960) reviewed the principal approaches to the problem of estimating ore reserves and suggested a new method based on the fact that the tonnage of minable reserves of the well-explored

elements in the United States at that time was roughly equal to their crustal abundance times 1 billion or times 10 billion.

I realize that abundance figures for some of the elements are still unproved, that reserve figures are always questionable, and that the assumption of log-normal distribution of trace elements in the earth's crust is not universally accepted. However, even rather large changes in abundance or reserve estimates will not affect the concepts discussed here.

Table 3 combines the abundance data of Lee and Yao and the reserve-abundance relationship of McKelvey with my own attempt at calculating the total amounts of several metals in the earth's crust, various segments of the crust, United States crust, United States crust to a 1-kilometer depth, and potential resources of recoverable ores.

Study of the table permits speculation about the position of the United States and the world with respect to mineral resources. For example, one could consider the total amount of an element present in the United States crust to a 1-kilometer depth as the ultimate United States resource of that element and portion it out by mineralogy or rock type. If an element tends to be lithophile, and thus occurs chiefly in silicate minerals, then a high percentage is probably forever unavailable as a resource. If an element is sulfophile, probably a greater amount is available as a resource. Or one might estimate, by working portion it out by mineralogy or rock type. If an element present at various grade levels in the United States crust to a 1-kilometer depth.

Table 3 shows that the most commonly sought metals, except lead, are more abundant in oceanic crust than in continental crust. This permits the speculation that perhaps we should make resource target maps showing the areas of the world where segments of oceanic crust are within reasonable exploration depths.

The part of the table showing resource potential

TABLE 3.—*Abundance, mass, reserves, and resources of some*

[Abundance in grams/metric ton (g/mt); mass and reserves in metric tons (mt).

Element	Total earth's crust				Oceanic crust		Continental crust		Continental crust segments: Shield areas	
	Goldschmidt [6] (g/mt)	Vinogradov [7] (g/mt)	Lee and Yao [8] (g/mt)	Mt×10 [12]	[8] G/mt	Mt×10 [12]	[8] G/mt	Mt×10 [12]	[8] G/mt	Mt×10 [12]
Antimony	1	0.5	0.62	14.9	0.91	8.1	0.45	6.8	0.46	4.9
Beryllium	6	3.8	1.3	31.2	.83	7.4	1.5	23.8	1.5	16.7
Bismuth	.2	.009	.0043	.1	.0066	.059	.0029	.041	.003	.029
Cobalt	40	18	25.	600	37	330	18	270	19	190
Copper	70	47	63	1,510	85	760	50	760	52	550
Gold	.001	.0043	.0035	.084	.0035	.032	.0035	.052	.0034	.035
Lead	16	16	12	290	10	90	13	200	13	.140
Lithium	66	32	21	500	20	180	22	320	21	220
Mercury	.5	.083	.089	2.1	.11	.9	.08	1.2	.078	.81
Molybdenum	2.3	1.1	1.3	31.2	1.5	14.6	1.1	16.6	1.1	11.6
Nickel	100	58	89	2.130	140	1,200	61	920	64	.680
Niobium	20	21	19	460	18	160	20	300	20	210
Platinum	.005	———	.046	1.1	.075	.67	.028	.43	.031	.30
Selenium	.09	.05	.075	1.8	.1	.89	.059	.91	.064	.64
Silver	.02	.07	.075	1.8	.091	.82	.065	.98	.067	.70
Tantalum	2.1	2.5	1.6	38.4	.43	3.8	2.3	34.7	2.3	24.3
Tellurium	.0018	.001	.00055	.013	.00088	.0078	.00036	.005	.00038	.0036
Thorium	11.5	13	5.8	140	4.2	37	6.8	.100	6.6	68
Tin	40	2.5	1.7	40.8	1.9	16.8	1.6	24	1.5	16.3
Tungsten	1	1.3	1.1	26.4	.94	8.3	1.2	18.1	1.2	12.7
Uranium	4	2.5	1.7	40.8	1	7.8	2.2	33	2.1	22.6
Zinc	80	83	94	2,250	120	1.030	81	1,220	83	870
	G/mt	G/mt	G/mt	Mt×10 [15]	G/mt	Mt×10 [15]	G/mt	Mt×10 [15]	G/mt	Mt×10 [15]
Aluminum	81,300	80,500	83,000	1,990	84,000	747	83,000	1,242	84,000	869
Barium	430	660	390	9.4	370	3.3	400	6.1	400	4.3
Chromium	200	83	110	2.6	160	1.4	77	1.2	81	.84
Fluorine	800	660	450	10.8	420	3.74	470	7.1	470	5
Iron	50,000	46,500	58,000	1,332	75,000	667	48,000	725	49,000	508
Manganese	1,000	1,100	1,300	31.2	1,800	16	1,000	15.2	1,100	10.6
Phosphorus	1,200	930	1,200	28.8	1,400	12.5	1,200	16.3	1,200	11.4
Titanium	4,400	4,500	6,400	153.6	8,100	72.1	5,300	81.5	5,500	57.1
Vanadium	160	91	140	3.36	170	1.61	120	1.85	120	1.3

[1] U.S. Bureau Mines (1970); 1 short ton =0.91 mt.
[2] Recoverable resource potential = 2.45 $A \times 10^6$ (abundance A expressed in g/mt).
[3] U.S. Bureau Mines (1970); 1 short ton =0.91 mt; does not include United States reserve.
[4] Recoverable resource potential =2.45 $A \times 17.3 \times 10^6$ (abundance A expressed in g/mt; land area of world is 17.3 times United States land area).
[5] U.S. Bureau Mines (1970); data on world basis.
[6] Goldschmidt (1954, p. 74–76).
[7] Vinogradov (1962, p. 649–660).
[8] Lee and Yao (1970, p. 778–786). All calculations are based on this work.
[9] Very high.

and ratio of potential to known reserves is particularly interesting and informative. The resource potential is calculated from the formula $R=2.45A\times10^6$ as explained below. The rationale for this calculation assumes that (1) McKelvey's relation of reserves to crustal abundance is valid, (2) U.S. Bureau of Mines reserve figures are of the correct order of magnitude, and (3) trace elements are log-normally distributed in the earth's crust. R is expressed in metric tons and A is expressed in grams per metric ton or parts per million. In the McKelvey formula, $R=A\times10^{9-10}$, R is expressed in short tons and A in percent.

Lead is used as the base of calculation because known reserves of minable lead ore already exceed $R=A\times10^{10}$. Continental crustal abundance of lead is 13 ppm or 0.0013 percent. Substituting in McKelvey's formula, $R=A\times10^{10}$, we get: $R=0.0013\times10^{10}=13\times10^6$ metric tons. Known United States reserves of lead are 31.8×10^6 metric tons or 2.45 times greated than $A_{Pb}\times10^{10}$. This factor (2.45) is greater for lead than for any other commonly sought metal except molybdenum, which has about the same factor. If we use assumptions 1 and 3 above, then currently recoverable resources of all trace elements should approach $2.45A\times10^6$. Obviously the 2.45 factor will increase as lead reserves of any other metal increase above $2.45A\times10^6$. Another very simple method of calculating potential recoverable resource assumes that the resource should approach 0.01 percent of the total amount of each element available in the United States crust to a 1-kilometer depth, as shown in table 3. It is important to remember that the McKelvey formula relates crustal abundance to currently recoverable reserves; therefore, my use of his formula restricts the calculated resource potential (table 3) to identified and undiscovered resources recoverable under present economic conditions. Paramarginal and submarginal resources as defined by McKelvey (1972)

metals in the earth's crust and in the United States crust

Calculations = mass (metric tons) × abundance (decimalized) = total content of element]

Continental crust segments—Con.					United States			World			
Folded belts		United States crust		United States crust to 1-km depth	Reserve [1]	Recoverable resource potential [2]	Ratio of potential to reserve	Reserve [3]	Recoverable resource potential [4]	Ratio of potential to reserve	Grade [5]
[8]G/mt	Mt×10 [12]	[8]G/mt	Mt×10 [12]	Mt×10 [9]	Mt×10 [6]	Mt×10 [6]		Mt×10 [6]	Mt×10 [6]		
0.43	1.9	0.45	0.41	11.2	0.10	1.1	11	3.5	19	5	Unknown.
1.6	7.1	1.5	1.4	38	.073	3.7	50	.015	64	4,000	
.0025	.012	.0029	.0025	.07	.013	.007	.5	.081	.12	1.5	
16	80	18	16	440	.025	44	1,760	2.14	763	360	
46	210	50	45	1,230	77.8	122	1.6	200	2,120	10	0.86 percent.
.0038	.017	.0035	.003	.085	.002	.0086	4.1	.011	.15	14	
13	60	13	12	330	31.8	31.8	1	.54	550	1,000	3 percent.
23	100	22	20	550	4.7	54	12	.78	933	1,200	
.086	.39	.08	.072	2.0	.013–.028	.20	16–6.8	.11	3.4	30	
1	5	1.1	1	27	2.83	2.7	1	2	46.6	23	Unknown.
53	.240	61	55	1,500	.18	149	830	68	2,590	38	1.5 percent.
19	90	20	20	550	Unknown	49	Unknown	Unknown	848	Unknown	
.022	.13	.028	.026	.71	.00012	.07	560	.009	1.2	133	
.071	.27	.059	.055	1.5	.025	.14	6	.695	2.6	36	
.062	.28	.065	.059	1.6	.05	.16	3.2	.16	2.75	18	
2.4	10.4	23	2.1	57.5	.0015	5.6	4,000	.274	97	354	
.00031	.0016	.00036	.00031	.0085	.0077	.0009	.11	.054	.015	.3	
7.1	32	6.8	6	.160	.54	16.7	31	1	288	288	Unknown.
1.7	7.7	1.6	1.4	38	------	3.9	[9] ?	5.8	68	12	0.6 percent.
1.2	5.4	1.2	1.1	30	.079	2.9	37	1.2	51	42	
2.3	10.4	2.2	2	55	.27	5.4	20	.83	93	112	
77	350	81	73	2,000	31.6	198	6.3	81	3,400	42	4 percent.

G/mt	Mt×10 [15]	G/mt	Mt×10 [15]	Mt×10 [12]	Mt×10 [6]	Mt×10 [6]	Ratio of potential to reserve	Mt×10 [6]	Mt×10 [9]	Ratio of potential to reserve
82,000	373	83,000	74.5	2,000	8.1	203,000	24,000	1,160	3,519	3,000
390	1.8	400	.37	10	30.6	980	32	76.4	17	223
68	.36	77	.070	1.92	1.8	189	387	696	3.26	47
480	2.1	470	4.30	11.8	4.9	1,151	235	35	20	600
4,000	217	48,000	43.5	1,200	1,800	118,000	65	87,000	2,035	23
930	4.6	1,000	.9	24.9	1	2,450	2,450	630	42	67
1,100	4.9	1,200	.98	26.8	931	2,940	3	16,000	51	34
5,000	24.4	5,300	4.9	1.30	25	13,000	516	117	225	2,000
110	.55	120	.11	3	.115	294	2,560	10	5.1	500

Calculation of mass of crustal segments

Total earth's crust ----------24×10^{18} mt.
Oceanic crust ----------8.9×10^{18} mt (37 percent of total crust).
Continental crust ----------15.1×10^{18} mt (63 percent of total crust).
Shield areas ----------10.6×10^{18} mt (30 percent of continental crust or 43.8 percent of total crust).
Folded belts ----------4.54×10^{18} mt (30 percent of continental crust or 19.1 percent of total crust).
United States crust ----------0.90×10^{18} mt (based upon United States as 1/17 of land area of world's continental crust).
United States crust to 1-km depth ----------24.6×10^{15} mt (based upon average thickness continental crust =36.5 km; therefore 1 km is 2.74 percent of United States crust).

are not included. (See "Introduction" to this volume.)

Some of the metals are listed in table 4 in order

TABLE 4.—*Ratio of potential resources to known reserves*

United States		*World*	
Pb	1	Sb	5
Mo	1	Cu	10
Cu	1.6	Pb	10
Ag	3.2	Sn	12
Au	4.1	Au	14
Zn	6.3	Ag	18
Sb	11	Mo	23
Hg	15	Hg	30
U	20	Ni	38
Th	31	Zn	42
W	37	W	42
Ni	830	U	112
Sn	Very high	Th	288

of increasing ratio of potential resources to known reserves, as shown in table 3. The ratios indicate, for example, that we can anticipate discovery of about 4 times as much minable gold ore as our present known reserves. Because lead was chosen as the base for calculating potential resources, its ratio is necessarily one.

It is interesting that for the United States those metals whose known reserves most closely approach the potential recoverable resources are the metals most diligently sought for the longest time (lead, molybdenum, copper, silver, gold, zinc). Although uranium is a relatively recently sought metal, the intensity of the search for it has moved its ratio close to the ratio of the traditionally sought metals. Thus, the scheme of predicting resource potentials in relation to crustal abundance seems valid—if we search for an element hard enough, we find it in about the quantities we might expect. The largest ratios, for nickel and tin, are caused by lack of known favorable host rocks in the United States. However, the large ratios suggest that we should take another look for these metals in the United States, but perhaps in different geologic environments from those in which we have traditionally looked. Commonly, the higher the ratio, the greater is the tendency for the element to form oxide or silicate minerals rather than the commonly sought sulfide ores.

Those metals with intermediate ratios are those that have not been vital to our economy in the past, or whose prices are subject to great fluctuation, or whose past source has been chiefly as a byproduct. But certainly these elements must also be present in the crust in crudely predictable amounts.

As we might expect, the ratios for world resources generally are much higher than United States ratios because many land areas of the world have not been intensely explored. Those few metals that do have lower potential ratios than the United States (antimony, tin, and nickel) are contained in old, well-known districts—the antimony of mainland China, the tin of Bolivia, Cornwall, and Malaysia, and the nickel of shield areas such as Canada and Australia.

Data on a few of the elements listed in table 3 deserve further comment. The tellurium ratio of potential resource to known reserve (0.11) indicates that we have 10 times more known reserves than predictable by $R=2.45\ A\times10^6$. Perhaps the crustal abundance figure is too low, but there is another, more important factor: most tellurium production comes as a byproduct of copper refining, and the known reserve figure for tellurium is equated with copper production and reserve (0.4 lb of tellurium per ton of copper produced). Therefore, copper ore that averages 0.86 percent Cu contains only 0.00017 percent tellurium. Thus we are in the unique situation of equating our known tellurium reserves to raw materials that contain only 1.7 ppm tellurium! Obviously rock containing 1.7 ppm tellurium, exclusive of other metals, could not be considered ore grade, and the relationship $R=2.45\ A\times10^6$ does not apply.

The same explanation holds for the low selenium (6) and bismuth (0.5) ratios. Selenium reserves also are equated with copper production (1 lb selenium per ton copper produced or about 4.3 ppm selenium in 0.86 percent copper ore). Bismuth reserves are equated to lead reserves (about 7 lbs bismuth per ton of western United States lead or 100 ppm bismuth in 3-percent lead ore).

Ratios that are extremely high can usually be explained by what we already know about the geochemistry and United States distribution of that element. Aluminum, for example, shows a very high ratio of potential resource to known reserve. Aluminum occurs chiefly in silicates, whereas currently minable aluminum ore (bauxite) is a weathering product and the vertical extent to which weathering can occur is limited. Thus much of the crust is removed from a possible resource category for aluminum until we can economically recover aluminum from feldspar or clay.

The high manganese ratio (2,450) results from a reserve figure based upon a 35-percent manganese concentrate produced by normal concentration methods. The word "normal" is the clue to the high ratio. The U.S. Bureau of Mines estimates that manganese deposits in the United States contain 68 million tons of manganese, but they are low grade and must be considered resources. However, if the

68 million tons were called reserve, then the ratio would be reduced to about 36.

Using the information in table 3, I have modified McKelvey's original diagram relating domestic reserves to crustal abundance (fig. 6). Domestic reserves of some metals have increased and new element-abundance numbers for continental crust are available since McKelvey first published this diagram in 1960. Because actual reserves of lead and molybdenum now equal 2.7 $A \times 10^{10}$, potential recoverable resources of the other elements also should approach this line. Note that the factor is 2.7 on this diagram and 2.45 on the table of abundance, mass, and reserves. This is because reserve tonnages on this figure are calculated in short tons to conform with McKelvey's original work. The 2.45 factor applies for the metric system. Of course, this line will continue to shift as additional reserves are discovered, but it does give us some broad measure of what we might expect.

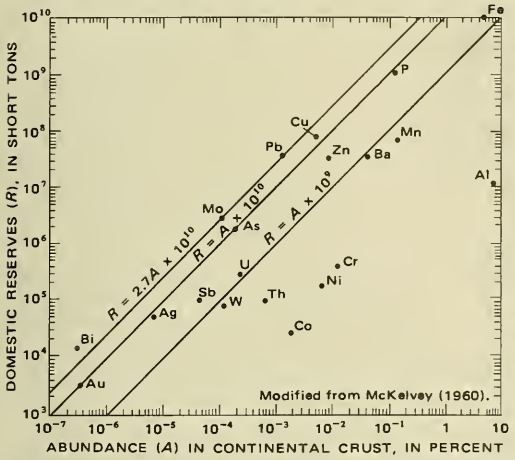

FIGURE 6.—Domestic reserves of elements compared to their abundance in the earth's crust. Modified from McKelvey (1960).

It is a simple fact, but often overlooked, that we cannot expect to find reserves or resources of the least abundant elements in the same magnitude as the more abundant elements. Thus, in a crude way, because copper is about 20,000 times more abundant than gold in the earth's crust, we can expect that recoverable resources of copper should be about 20,000 times greater than recoverable resources of gold. This simple relationship, of course, is modified by the inherent geochemical nature of each element.

If we accept the abundance-reserve relationship, it follows that $R=2.45\times10^6$ is a minimum total resource estimate because the relationship is based upon *currently recoverable* resources and does not include resources whose feasibility of economic recovery is not established. Total resource estimates of an element that vary substantially from this formula probably are caused by geologic factors and the inherent geochemical nature of the element. However, the discovery of Carlin-type gold deposits, Spor Mountain beryllium deposits, and Precambrian Belt Supergroup copper deposits, all in the last decade, indicate that we need to critically examine our criteria for where and how to look for mineral deposits. Certainly, significant mineral deposits remain undiscovered because exploration efforts are commonly confined to the classic environments of ore deposition.

As analytical techniques improve, as our understanding of geochemical processes improves, and as exploration methods improve so that we can confidently explore and examine the crust to a reasonable depth, the reserve-resource-abundance relation should become more closely defined. Perhaps then we can determine whether ore deposits are chiefly formed by different ore-forming processes in a uniform crust or because of differences in original composition of crustal segments.

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ABRASIVES

By Robert E. Thaden

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ABSTRACT OF CONCLUSIONS

Abrasives are substances used to clean, dress, or comminute other substances. They are of critical importance to the economy of industrial nations. The principal natural abrasives are diamond, corundum, emery, garnet, tripoli, and silica sand, and the United States is fortunate to have identified resources of most of them which will serve as supply at current rates of consumption for from 50 years to more than 100,000 years. The United States has no commercial deposits of diamond, but manufactured diamond already satisfies more than one-half of the domestic requirements. Other artificial abrasives, principally aluminum oxide, silicon carbide, and steel shot and grit, manufactured from abundant raw materials, have supplanted natural abrasives in about 90 percent of all critical applications and, together with "artificial" diamond, encroach on the few remaining uses for which the natural abrasives in shortest supply once were thought uniquely qualified.

INTRODUCTION

Abrasives are those substances that are used to clean or dress the surfaces of other materials, or to comminute other materials by abrasion and percussion. Because of their great differences in hardness, abrasives have many thousands of applications.

The deliberate removal of solid material by abrasive action consumes the bulk of all hard abrasives. This includes such diverse operations as grinding valve seats with abrasive-charged paste, sharpening tool blades with appropriately shaped abrasive stone blocks, grinding and polishing bearing surfaces on machine components with bonded granular abrasive wheels, sandblasting inscriptions on tombstones, and slabbing and drilling rock with abrasive-charged discs, wires, and drill bits.

The cleaning function employs abrasives softer than the material being cleaned to remove a surface film of foreign material with minimal damage, as in brushing the teeth with dentifrice, or in scouring porcelain bathroom fixtures or automobile paint with abrasive soap.

Comminution can be effected by heavy abrasive wheels or by abrasive pebbles tumbling or cascading in a mill. By the latter process, ores, for example, are reduced to the size required for their further metallurgical treatment, small parts are deburred, wheat is ground to flour, and talc and paint pigments are ground to the size appropriate for their ultimate use.

Strictly speaking, neither sandblasting nor the crushing of ore by cascading pebbles of shot are abrasive operations, inasmuch as the action is one of percussion. Nevertheless, these processes are included here not only because both the "abrasive" materials and the effects are the same as though the operations had been accomplished by abrasive action, but because historically the abrasives used in percussive applications have not been differentiated in tables of production statistics from the same materials used for true abrasive purposes.

The first applications of loose grains of quartz and of quartz sandstone and other naturally bonded

stones for abrasive purposes are lost in prehistory. Early in the first millennium B.C., the hard natural abrasives diamond, corundum, and garnet already were known, at least in India and Greece. By A.D. 1500, the artificial bonding of loose natural abrasive grains was introduced, first as sheets and later as blocks and wheels. The first bonding agent was shellac, the next was rubber, and in the last half of the 19th century. synthetic resins, metals, and ceramics were introduced. When powered grinding equipment became available about 1860, the use of abrasives assumed a large role in metalworking operations that had been accomplished previously by saws, chippers, shapers, lathes, and milling machines, but the major surge in the use of abrasives came about 1900 with the commercial introduction of the first of the artificially produced hard abrasive materials, aluminum oxide and silicon carbide. The use of steel rod and shot as pulverizers in tumbling mills and of steel grit as a sandblast medium also was introduced about 1900. Artificial aluminum oxide and silicon carbide, mostly used for dressing metals and slabbing stone, have dominated the market for hard abrasives for many years and currently account for about 90 percent of all the hard abrasives used in this country.

The continued use of certain natural abrasives testifies to their desirable qualities as yet poorly matched by the artificial abrasives and to their lesser cost per unit of work. It is not to be expected, however, that those natural abrasives which still dominate a few specialized applications will continue to retain their fairly exclusive use. As Coes (1971, p. 33) insisted.

> corundum and emery * * * [and] several other natural minerals are used as abrasives although their total value is only a small fraction of the value of the synthetic abrasives used. Furthermore, their usage is highly specific. In time, existing synthetic abrasives will probably replace all of these, but the economic incentive is now lacking to work out the techniques for using them * * *. To replace these natural agents by new synthetic materials is probably quite possible, but the size of the market has, so far, seemed inadequate to justify the necessary research. Development of such synthetics probably must wait for the exhaustion of the supply of natural material or a substantial increase in its cost. At the moment this situation does not seem imminent * * *.

In general, the need for hard abrasives in industry in the United States is overwhelmingly satisfied by synthetic, not natural, materials, and the trend toward lower demand for natural abrasives will continue. Modern technology is increasingly devoted to automatic machinery operated at high speeds and high pressures to produce finishes of high precision and is, therefore, correspondingly dependent upon the uniformity inherent in the artificial abrasives as well as upon their capability of being tailored to specific needs—characteristics not shared by the natural abarsives. Industry is not dependent upon the naturally occurring materials. All natural abrasives currently in use can be replaced by artificial abrasives after a short changeover period or after minor research, should the need arise. Nearly all the current consumption of natural abrasives is dictated by tradition or by cost—principally by cost—and not by the unique qualities or the availability of the abrasives, so whether or not the United States has vast resources of the natural abrasives is largely of academic interest. The artificial abrasives, of course, are derived from natural materials, but resources of these materials seem to be abundant.

THE NATURAL ABRASIVES

The number of naturally occurring abrasive substances commonly in use is large. These substances represent more than 30 different mineral species and of some species, many varieties. The principal hard natural abrasives are diamond, corundum, emery, and garnet. Staurolite, kyanite, sillimanite, epidote, andalusite, topaz, bertrandite, and other hard minerals may have, or may have had, a minor and occasional local use. Natural abrasives of moderate hardness include the silica minerals, quartz (including quartz sand and river silt), chert, flint, jasper, chalcedony, tripoli, diatomite, and rottenstone; the feldspars; the volcanic glasses, pumice, perlite, and obsidian; and rocks such as basalt, granite, and quartzite, mostly used as grinding pebbles. A few of the more common abrasives of inferior hardness are apatite, dolomite, calcite (including chalk and whiting), clays, and talc.

Not many of the natural abrasive substances are valuable enough to be transported long distances. Most are abrasives of opportunity, generally termed "regional" abrasives. They are consumed close to the point of production to the exclusion of other abrasives far more efficient but far more costly. Examples of some of these regional abrasives are quartz sand—several million tons of which is consumed annually, river silt, ground limestone, and ground feldspar. The resources of these materials relative to their local consumption are virtually unlimited. Only a few of the naturally occurring abrasives deserve individual description. These are the abrasives that are reputed to have certain desirable qualities and applications to specialized purposes, that are costly or in short supply, or that are not readily replaced by artificial abrasives.

DIAMOND

Diamond, carbon crystallized in the cubic system, is the hardest natural substance known. Of all the diamond produced, only a small fraction is suitable for gemstones owing to inclusions, polycrystallinity, twinning, unpleasing color, or other flaws. The material unsuitable for gemstones is used in industry. Only a small portion of industrial diamond goes into manufactured goods such as phonograph needles, instrument bearings, and wire-drawing dies; most is used for abrasives. Pencillike tools for scribing or cutting glass, or for truing and dressing abrasive wheels, have a whole diamond crystal or a large fragment set into the face of the tool. Rock drills also have their working faces implanted with diamond crystals, commonly in an annular pattern at the end of a steel pipe. By rotating the pipe, a cylindrical core of rock can be cut from the earth for inspection. Most industrial diamonds are crushed to powder and used in a slurry of oil or water for faceting gems—especially diamond, which can be abraded by virtually no other material, drilling holes in instrument bearings, or polishing optical parts; some are bonded to wheels or disks and used for such purposes as slabbing rock, sharpening carbide and other hardfaced tools, and precision-grinding hard ceramic forms to tolerances of a few millionths of an inch.

Diamond abrasive is of critical importance to industry. Until 1955, the entire supply was imported because the United States has no commercial deposits of its own. In 1955, a commercial process for producing artificial industrial diamonds was perfected in the United States. Production in the United States now is in excess of 15 million carats annually, and it continues to rise. It is supplemented by at least three other manufacturers throughout the world. The drop in imports of natural industrial diamond by the United States has not yet matched the rise in production of artificial diamonds because of increasing industrial activity and the discovery of new applications for abrasive diamond. Imports have dropped, however, from a high of about 20 million carats to about 13 million carats (about 3 tons) annually and are expected to drop further as economics and the increasing capabilities of the existing and anticipated manufacturers of artificial diamond allow.

Most imported diamond comes from the Union of South Africa, but because a single distributing corporation markets nearly 90 percent of the world diamond production, the purchase of large lots of industrial diamond probably implies the inclusion of small quantities from such other diamond-producing countries as Angola, Congo, Rhodesia, Ghana, Guinea, Ivory Coast, Liberia, Sierra Leone, South-West Africa, Tanzania, Brazil, Guyana, India, Indonesia, and Venezuela. Diamond is known in the Soviet Union in the Ural Mountains and at the recently discovered deposits near Yakutiya; but little, if any, Soviet diamond comes to the world market.

Natural diamond normally occurs only in an unusual type of peridotitic igneous rock known as kimberlite which was injected into overlying rocks mostly as cylindrical bodies, or "pipes," from deep in the crust of the earth. Of several hundred pipes known throughout the world, only a few contain diamonds, and of these only a few contain diamonds in commercial quantity. Two kimberlite pipes are known near Murphreesboro, Ark. One contains uneconomic quantities of diamond; the other, apparently, no diamond. Although diamond has been found in at least half the States, neither the original diamond-bearing pipes nor the alluvial placer concentrations derived from them have been discovered. The few stones found in the North-Central States probably were carried south from undiscovered Canadian sources by the continental glaciers of the fairly recent past.

It is at least possible that diamonds can form in highly metamorphosed rock; these are common in the Southeastern States, California, Montana, and elsewhere where diamonds have been found. But ultramafic rocks also are known in these areas, and kimberlite pipes cannot be ruled out as the sources of these diamonds simply because they have not yet been discovered. Usually neither the topographic expression of pipes nor the surface appearance of weathered kimberlitic material is so exceptional as to indicate readily the presence of pipes, and the pipes are easily hidden by surficial material because they do not cover large areas—the largest diamond pipe known in the world covers barely 350 acres. Perhaps the best way to prospect for kimberlites or other diamondiferous rocks is to pan stream samples for diamonds, which are heavy and remain in the concentrate, and especially to look for those other few heavy and unusual minerals that almost universally accompany diamond—chrome diopside and pyrope garnet, together with the more common ilmenite.

CORUNDUM

Corundum is aluminum oxide crystallized in the hexagonal system. After diamond it is the hardest known natural substance. Two forms of corundum are common: (1) prismatic crystals which range in size from sugary aggregates to large crystals that

commonly taper from the middle toward each end and exhibit a pronounced transverse parting, and (2) large polycrystalline blocks. Corundum crystals normally are translucent or opaque white, gray, blue, red, brown, black, or green, but some are transparent red, pink, blue, or bluish-green, or exhibit asterism or other pleasing chatoyancy, and these are valued as gemstones known to the jewelry trade as ruby and sapphire.

Abrasive corundum is used nearly exclusively as crushed, carefully sized grit and powder for finishing optical parts and for lapping and polishing metals. The transverse parting characteristic of much corundum presents to the work a sharp, chisel-like edge which scrapes rather than scratches the work and produces a smooth surface. When the abrasive wears, a flake spalls off so as to expose a new sharp chisel edge. Probably it is this characteristic that encourages a continuing small demand for corundum despite the fact that garnet, diamond, artificial aluminum oxide, and other abrasives can successfully substitute for all the uses to which corundum is now put.

About 2,000 tons of corundum is imported each year, and about one-tenth of this is reexported as prepared grinding powder. For many years the source of supply was Rhodesia, but political considerations in mid-1968 cut off this supply, encouraging many users of corundum to convert immediately — and probably permanently — to artificial abrasives. South Africa has become the new source. It is perhaps a measure of the relative unimportance of corundum in our economy that the long-term Rhodesian source was cut off only a few months before the U.S. Government removed corundum from the list of strategic materials and offered for sale the last 2,000 tons of corundum in the strategic stockpile.

The United States has no reserves of corundum, and the resources are poorly known. Not much more than 10,000 tons was produced between 1870 and 1906; none has been produced since that time except for small test lots during the World Wars. Probably the one area in the United States containing the largest amount of potential corundum ore is that area embracing Clay, Macon, and Jackson Counties, N.C., and Towns and Rabun Counties, Ga., although corundum also is known in all of the Appalachian States, from Maine to Alabama, and in a few places in California, Montana, and Idaho.

Deposits of corundum in the contact zone between peridotitic intrusive rocks and enclosing highly aluminous metamorphic rocks, especially those in Georgia and North Carolina, were the principal source of corundum in the United States. The genesis of these deposits has been debated by geologists for many years. Corundum also is a constituent of placer deposits and of more than 20 kinds of igneous rocks, including granite pegmatite, nepheline syenite, anorthosite, and gabbro. In some gneisses and schists, corundum makes up from 5 to 60 percent of the material in zones that range from a few inches to several tens of feet in width and that may extend several miles, although no such concentration currently represents an economic deposit. Panning would seem to be the method of choice for prospecting, and although perhaps not applicable to deposits in the United States, prospectors should be aware that peridotites rich in chromite generally contain no corundum, whereas those without chromite may.

EMERY

Emery is a gray to black granular material consisting of corundum and magnetite with admixed spinel, hematite, garnet, and other minerals. The proportion of some constituents ranges widely; some specimens are nearly pure corundum, others nearly pure magnetite, and still others nearly pure spinel.

Synthetic abrasives have reduced the formerly multiple uses of emery to two. About 3 percent currently is made into coated abrasive sheets; the rest is used in nonskid pavements and stair treads. The true emery wheel has now become an antique curiosity. Only custom and economics encourage the continued use of emery because manufactured aluminum oxide grain probably would be superior for the same applications. Even granular magnetite, hematite, spinel, or garnet may substitute adequately, as indeed they probably have, judging from reported variations in the mineral content of emery ore used in the past.

Emery deposits are known in New York, Massachusetts, Virginia, North Carolina, and Pennsylvania. Those in New York, a group of deposits about 3½ mi southeast of Peekskill and concentrated within an area of about 1 square mile, probably represent the largest single source in the United States. The U.S. Bureau of Mines estimated reserves of these deposits in 1955 at 60,000 tons, but since then the entire U.S. production of about 150,000 tons has been from these deposits and production continues from a single mine at an annual rate of 5–10 thousand tons. The extent of surface openings indicates that, with full development and the accommodation of several grades of ore, these deposits may well be capable of producing more than 10,000

tons per foot of depth to depths of many hundreds of feet. Overseas supplies have come from Greece and Turkey at an annual rate of from a few hundred tons to about 2,000 tons. Reserves in these countries aggregate 5–10 million tons and the resources probably amount to many millions of tons. Large deposits of emery are known in the Soviet Union, but this emery does not enter world trade.

Emery deposits in Greece and Turkey occur as pods and lenses in metamorphosed limestone; those in the United States are in the margins of mafic intrusive rocks which are in contact with aluminous country rock. All probably result from contact-metamorphic processes, although geologic controversy very similar to that involving corundum deposits also has accompanied the study of deposits of emery.

GARNET

Garnet is the term applied to about 15 varieties of a complex silicate mineral which crystallizes in the cubic system, generally as rhombic dodecahedra. This form is nearly spherical and gave rise to the name garnet, derived from the Latin "granatus," meaning grainlike or seedlike. Common commercial garnet is almost entirely the variety almandite, a dark-red to dark-brownish-red iron aluminum silicate.

Garnet currently has three major uses as an abrasive. (1) About 45 percent is used as a sandblast medium to clean an impart a textured surface to both ferrous and nonferrous metals in the shipbuilding, aircraft, and automotive industries, and to a much lesser extent for such other manufactures as home appliances, stone, and artworks. The tough round alluvial garnet crystals impart a pleasing work-hardened matte surface to these materials. (2) About 35 percent is used as crushed grit and powder to grind and polish lenses and other optical parts, to surface semiconductor materials, and to accomplish the intermediate grinding in the finishing of plate glass. The recent advent of the Pilkington, or "float," process of plate-glass manufacture, whereby a ribbon of hot glass is drawn across a bed of molten tin resulting in a finished surface of plate-glass quality, will probably reduce substantially the future demand for crushed and sized garnet grit for glass-grinding purposes, currently about 4,000 tons per year. (3) About 20 percent is crushed and made into abrasive sheets. In this form it is used to dress rubber, plastics, leather, soft metals, and wood.

The use of garnet as an abrasive is almost entirely American; more than 95 percent of the garnet produced in the world is produced in the United States, and more than 80 percent is consumed here. Yet there are only two producing mines of consequence, and total annual production is only about 20,000 tons. Spain, Portugal, India, and Canada have produced small quantities very occasionally.

The garnet from New York State has an unusual structure, a closely spaced lamellar parting ordinarily not developed in garnet, that results in chisel-edged granules when the garnet is crushed, which scrape the work surface rather than scratch it. This property makes the garnet similar to corundum, for which it commonly substitutes. This garnet is unmatched as a tool for surfacing furniture woods or soft metals, or for skiving leather and rubber, and its use for grinding glass results in fewer scratches and a lower rejection rate than does use of other abrasives. Yet, garnet has no application in which it cannot be replaced by other appropriately prepared and adapted abrasives, ranging from sand, glass beads, and steel grit for sandblasting, to diamond powder for finishing optical parts. A continuing, even moderately increasing, use of garnet is probable, subject nearly entirely to changes in economics and technology.

Garnet, as a source of commercial abrasives, occurs almost exclusively in metamorphic rocks and in placer deposits derived from them. Garnet-rich zones in gneisses and schists may contain 4–60 percent garnet, may be several hundreds of feet wide, and may extend for many miles. Many placers contain as much as 20 percent garnet, and very few beach, dune, glacial, and stream deposits throughout the world do not contain from a fraction of a percent to a few percent of garnet. The garnet easily could be saved by any of several simple mechanical or electrical methods of extraction, but it almost never is; large quantities of garnet are lost every day in the production of sand and gravel from these deposits for other purposes. Garnet deposits have been reported in more than half the States—all the States west of the Great Plains—and the Appalachian States from Maine to Georgia. The alluvial sandblast garnet recovered from Idaho comes from a single placer deposit estimated to contain 500,000 tons of recoverable garnet. There are unmined placers in the Western States, and perhaps some undiscovered placers. The garnet with the lamellar parting currently being mined from a coarsely crystalline gneiss at North Creek, N.Y., is in a deposit which if fully developed could produce more than 7,000 tons of garnet per foot of depth to a depth perhaps in excess of 1,000 feet. Several other deposits of garnet with lamellar partings are reported elsewhere in northern New York, in New

Hampshire, and in North Carolina. Those in North Carolina apparently are very large. Nonlamellar garnet also is common in metamorphic rocks and in placer deposits in the Eastern States, particularly in the Adirondak Mountains of New York State. Many of these deposits have been little prospected, and the resources are not well known, but it is certain that each of a reasonably large number of deposits contains from half a million to many millions of tons of garnet. Overseas resources of garnet are unknown, inasmuch as garnet is little used outside the United States.

SILICA SAND

Silica sand, both crushed and uncrushed, is used in large quantities; one-half million tons is used in this country annually for grinding stone and glass, and more than a million tons for sandblast purposes. It is, or could be, produced in each of the 50 States by nearly any of the more than 5,000 producers of sand and gravel currently operating. Resources are large. (See chapter "Silica.")

TRIPOLI

Tripoli is fine-grained silica which remains as a bedded residuum of the weathering of siliceous limestone. It is roughly similar in characteristics and uses to rottenstone, mined in Pennsylvania from weathered siliceous shale, and to diatomite, bedded deposits of the siliceous remains of marine microorganisms. A combined total of about 40,000 tons of these materials is consumed each year as abrasives, mostly in scouring soaps and powders and in metal- and lacquer-polishing pastes. Large deposits of tripoli are known in Illinois, Missouri, Oklahoma, Tennessee, Georgia, Alabama, Arkansas, California, Texas, and Nevada. Deposits of diatomite are known in several Western States. (See chapter "Diatomite.")

THE ARTIFICIAL ABRASIVES

After the commercial introduction of artificial abrasives about 1900, the industry became almost immediately dominated by these products. The dominance is increasing even today. Aluminum oxide in particular found its principal application, among a host of other applications, in the rough grinding of ferrous metals, an operation formerly accomplished slowly and expensively by metalworking machinery. Nearly all subsequent research on artificial abrasives has been directed to the discovery of an abrasive even more efficient than aluminum oxide for grinding ferrous metals. None has been found, although large families of carbides, borides, nitrides, silicides, oxides, and even a few artificial silicates have been tried. A few abrasives useful for other purposes have been discovered, and research continues.

Artificial diamond, as discussed above, was first produced in 1955. It is manufactured from a mixture of graphite and a catalyst of iron, manganese, chromium, cobalt, nickel, or other metal under conditions of high temperature and pressure, typically 3,000°C., 70,000 bars of pressure, and several hours of time. Although available for less than 20 years, artificial diamond already infringes seriously on the market for natural industrial diamond, all of which must be imported. This trend is expected to accelerate in the years ahead. Artificial diamond itself may one day be challenged as an abrasive because artificial cubic boron nitride, invented in 1957 and manufactured in much the same way as diamond, has been demonstrated in grinding tests to abrade diamond as rapidly as does diamond. It also has the advantage of remaining stable at high temperatures, whereas diamond tends to revert to graphite at the temperatures often reached at the grinding surface, resulting in rapid ablation of the diamond in the abrasive wheel. Diamond also is difficult to incorporate in ceramic-bonded wheels because of high-temperature effects.

Artificial aluminum oxide, chemically but not physically identical with corundum, is manufactured by fusing or sintering bauxite or intermediate products in an electric furnace. Annual production is more than 200,000 tons and requires about 320,000 tons of bauxite, or about 2 percent of the annual consumption of bauxite in the United States. Ten to fifteen percent goes into nonabrasive applications, mostly refractory products. New techniques over the years have lowered the required alumina content of the furnace charge, previously 60 percent, to less than 50 percent, and further technological changes are expected soon to allow alumina contents of only 35 percent, making available vast resources of syenitic and other aluminous rock for this purpose.

Commercial production of silicon carbide is accomplished by the reaction of a mixture of silica sand and coke, preferably petroleum coke, in an electric furnace. The principal abrasive use of silicon carbide is in the wire sawing of stone, but the abrasive successfully substitutes in many operations to which hard natural abrasives also are put, including the skiving of rubber and leather, and it is the leading abrasive in the dressing of nonferrous metals. Nearly 200,000 tons of silicon carbide is produced each year in the United States, about half of which is used as an abrasive. Refractory appli-

cations require most of the rest.

Steel, as shot and grit, is used extensively as a sandblast medium and as pebbles in tumbling mills. More than 200,000 tons is produced for these purposes each year. This amount requires the furnace reduction of about 400,000 tons of iron ore.

Other artificial abrasives are manufactured in relatively small amounts. Many are furnace products and are made in much the same manner as aluminum oxide and silicon carbide. Among these are zirconium oxide, cerium and other rare earth oxides, and rouge and crocus (iron oxide for polishing). Others are precipitates from aqueous solutions and several of these, including calcium carbonate and silica, duplicte the naturally occurring minerals and are used for the same purposes.

POTENTIAL RESOURCES

Resources of the several abrasive materials in the United States range from the infiinitesimal to quantities which for practical purposes approach the infinite. There are no known diamond deposits and little prospect of discovering any, but deposits of silica sand are literally underfoot in many parts of the country. The size of deposits of other abrasives lies between these extremes.

Table 5 gives estimated tonnages for each of the more significant abrasive materials occurring in the United States. Estimates of identified resources are based on the general premise that a tabular deposit, one with great length and depth relative to its width, should conservatively produce ore from a volume of rock that is six times the volume of an equidimensional quarry opened to the full width of the deposit. Most corundum and garnet and much emery characteristically occur as concentrations within lenticular zones in metamorphic rocks having these dimensions. Podlike deposits such as those formed marginal to intrusive bodies are estimated to produce ore to a depth equivalent to the longest surface dimension of an individual ore body of average size. Bedded deposits are estimated to produce half as much ore as is indicated by the lateral limits and the average thickness known from extensive outcrop, drill, or mining exploration.

TABLE 5.—*Resources, in short tons, of abrasive materials in the United States*

Commodity	Identified resources [1] (including reserves [2])	Hypothetical resources [3]
Diamond	0	0
Corundum	125,000	>2,000,000
Emery	3,000,000	>4,000,000
Garnet	14,000,000	>100,000,000
Triopli (and related materials)	4,500,000,000	>10,000,000,000
Silica sand	Large	Large

[1] Identified resources: specific, identified mineral deposits that may or may not be evaluated as to extent and grade, and whose contained minerals may or may not be profitably recoverable with existing technology and economic conditions.
[2] Reserves: identified deposits from which minerals can be extracted profitably with existing technology and under present economic conditions.
[3] Hypothetical resources: undiscovered mineral deposits, whether of recoverable or suheconomic grade, that are geologically predictable as existing in known districts.

The apparent large quantities of identified and hypothetical resources of the several abrasive materials relative to their annual consumption makes an estimation of tonnages of speculative resources superfluous.

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UNITED STATES MINERAL RESOURCES

ALUMINUM AND BAUXITE

By Sam H. Patterson and John R. Dyni

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ABSTRACT OF CONCLUSIONS

Imports of bauxite and alumina, mainly from Jamaica, Surinam, and Australia, supply approximately 87 percent of the United States requirements for manufacture of aluminum metal and certain refractories, abrasives, and chemicals. Bauxite mined in Arkansas, Georgia, and Alabama supplies the remaining 13 percent. Barring unforeseen political developments, the growing requirements of the aluminum industry in the United States will be met by imports of increasing amounts of aluminum metal and alumina rather than bauxite ore.

Domestic resources of bauxite—approximately 40 million tons reserves and 250–300 million tons potential resources—are inadequate to fulfill the long-term demand; however, the Nation has virtually inexhaustible potential resources of aluminous materials other than bauxite. High-alumina clays now seem the most promising of the potential alternate sources of aluminum. Dawsonite in the rich oil-shale deposits of Colorado is a possible source of aluminum that may be a recoverable byproduct of shale oil. Alunite, reportedly found in a large deposit in Utah, may be a possible source of aluminum and other products. Other less promising potential resources include aluminous shale and slate, aluminum phosphate rock, igneous rocks, saprolite, coal ash, and copper-leach solutions.

Exploration for major high-grade bauxite deposits should continue. Favorable areas for exploration include parts of South America, Africa, Asia, and Australia. Use of improved analytical tools, such as the borehole neutron activation probe, could speed up exploration for new deposits and evaluation of known deposits. Geologic research is also needed on the nonbauxite sources of aluminum in the United States, inasmuch as the detailed geologic information available on the potential resources is inadequate.

INTRODUCTION

Aluminum is a silvery white ductile lightweight (specific gravity of 2.7) metal having efficient electrical conductivity and resistance to oxidation. Because of its properties, abundance, and low cost, aluminum has become one of the most important metals in industry; only iron surpasses it in tonnages used. Major uses of the metal are in the construction industry and in the manufacture of aircraft, motor vehicles, electrical equipment and supplies, fabricated metal products, machinery, beverage cans, containers, and a wide variety of home-consumer products. Aluminum is essential to our standard of living and is a strategic commodity

for military defense. Plastics, wood, and other metals including copper, steel, lead, zinc, magnesium, and titanium could be substituted for some of the uses for aluminum. However none of these materials has all the properties of aluminum, and none offers much market competition for aluminum, except for a few specialized uses. Both alumina (the oxide of aluminum, Al_2O_3) and bauxite (the major ore of aluminum) are used in the manufacture of refractories, abrasives, and chemicals.

Bauxite is a complex impure mixture of aluminous minerals, chiefly aluminum hydroxides. Alumina content of most bauxites ranges from 35 to 50 percent; the common impurities are quartz, kaolinite, and iron-oxide-bearing minerals. Bauxite ores, of which there are several types, are classified by mineral content, occurrence, use, and source. In recent years, about 88 percent of the bauxite and alumina consumed in the United States was used in making metal, 4 percent in refractories, 6 percent in chemical and related uses, and 2 percent in abrasives.

Aluminum metal is made by extracting alumina from bauxite by the Bayer process and by reducing this oxide to metal electrolytically. In the Bayer process, bauxite is leached under pressure and heat by a caustic solution which converts the ore to a solution of sodium aluminate and red mud waste. From this solution, hydrated aluminum oxide is precipitated, washed, and calcined to obtain alumina. This alumina is then reduced to the metal by electrolysis of a hot molten solution of alumina and crolite, Na_3AlF_6. Metallurgical-grade bauxite ranges from 35 to 55 percent Al_2O_3. Depending on grade and type of ore, between 4.7 and 7 short tons of bauxite are required to produce 2 tons of alumina, and 2 tons of this oxide are required to make 1 ton of aluminum metal.

Bauxite used for manufacture of abrasives, refractories, and chemicals must meet more restrictive specifications as to aluminum, silicon, iron, and titanium contents than does metallurgical bauxite (table 6). Although the amount of bauxite used for purposes other than metal production is relatively small, these uses are of major importance to industry. For example, only 2 percent of U.S. bauxite consumption is used to manufacture aluminum oxide abrasives; yet this represents about half of all production of artificial abrasives and more than five times the total production of natural abrasives.

TABLE 6.—*Specifications, in percent, for abrasive, chemical, and refractory grades of bauxite* [1]

Grade	Al_2O_3	SiO_2	Fe_2O_3	TiO_2
Dried:				
Abrasive	Min 55	Max 5	Max 6	Min 2.5
Chemical	Min 55–58	[2] Max 5–12	Max 2	----------
Refractory	Min 59–61	Max 1 5–5.5	Max 2	Min 2.5
Calcined	85–90	3–6	1.5–7.0	3–4

[1] Modified from Stamper (1970, p. 440)
[2] A major portion of the bauxite used by the U.S. chemical industry exceeds 15 percent SiO_2.

The United States is dependent mostly on imports for its bauxite and alumina requirements. Excluding trade in alumina metal, the United States in 1971 produced about 2 million long dry tons of bauxite, imported 13.7 million long tons of bauxite and 2.3 million short tons of alumina, and exported 30,000 tons of bauxite, and 1.1 million tons of alumina. In that year, the United States consumed the equivalent of approximately 27 percent of the world production of bauxite and produced domestically only 12.5 percent of its requirements. Between 1967 and 1970, imports of bauxite were from Jamaica (59 percent), Surinam (24 percent), and other countries (17 percent). Alumina imports during the same period came from Australia (52 percent), Surinam (24 percent), Jamaica (18 percent), and other countries (6 percent).

UNITED STATES AND WORLD BAUXITE PRODUCTION

Aluminum was extracted from bauxite in both France and England in the middle of the 19th century, but less than 50 tons of metal had been produced by 1885. Production increased at a rapid rate in the late 1800's; the yearly world demand for bauxite, however, did not reach 1 million tons until 1917, during World War I. World production of bauxite dropped sharply after the war and reached a low of 334,000 tons in 1921. A little more than 1 million tons was produced in 1923, and a yearly production of 2 million tons was first reached in 1929. World production again dropped in the depression years of the early 1930's (fig. 7) but recovered in the last half of the decade and reached a sharp peak of more than 13 million tons in 1943. Production again slumped sharply after World War II as the economy changed to peacetime conditions and accumulated stocks were consumed. After recovering from this slump, world production reached 11 million tons in 1951 and has since remained on a sharply increasing trend, reaching 57 million tons in 1970.

Domestic production, including the World War I peak, remained below 1 million tons annually until very intensive mining was started in 1942 to meet World War II requirements; a record production of 6.2 million tons was reached in 1943 (fig. 7).

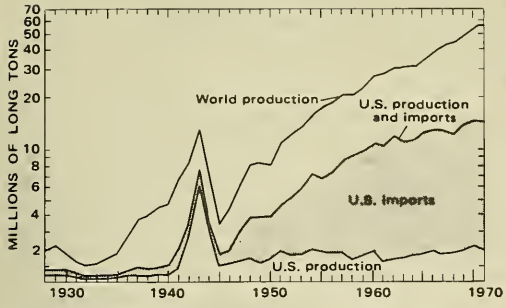

FIGURE 7.—United States production and imports and world production of bauxite, 1928–71 (1971 world production is inferred), compiled from U.S. Bureau of Mines Minerals Yearbooks and statistical data.

Since that war, production has remained between 1 and a little more than 2 million tons a year.

The Arkansas district has produced more bauxite than all other districts in the United States combined. About 64 million tons was produced in Arkansas from 1896 through 1971. Production in all Southeastern States from 1889 through 1971 amounted to only 3.6 million tons, dry basis.

BYPRODUCTS

A few metals and other byproducts are recovered in making aluminum. Gallium is recovered from Arkansas bauxite by one company and from bauxite in Hungary. Pig iron is produced from bauxite processed by the Pedersen method in Norway. Vanadium has been recovered from bauxite in France. Vanadium and chromium were produced from bauxite in Germany during World War II. Red mud, the waste product from the Bayer process, has been used as a soil conditioner to neutralize acid soils in Arkansas and as a red pigment in foreign countries. Phosphate and portland cement are coproducts of alumina recovered from nepheline syenite in the U.S.S.R. Some bauxite resources in the United States and large bauxite deposits elsewhere in the world contain substantial amounts of titanium. Although there has been considerable research on recovery of titanium from bauxites, its extraction has not yet proved to be profitable.

ENVIRONMENTAL CONSIDERATIONS

Like the other mineral and metal industries, the aluminum industry faces serious environmental problems. Those related to mining are primarily the reclamation of strip-mined land and the contamination of streams by sediment. Those related to recovery and use include (1) disposal of red-mud waste from alumina plants, (2) control of atmospheric contamination by dust and fumes containing fluorides, and surface-water contamination from electrolytic plants, (3) the control of sulfur in fuel for the generation of electricity, and (4) disposal and recycling of used metal. The industry is making significant progress on environmental problems, though improvements are still to be made. The reclamation of recently mined lands is efficient. In most plants, scrubbers are in operation to clean up gaseous effluents, monitoring systems are installed to check their continued efficiency, and water is treated to control toxicants. However, the big problem of disposal or profitable use of red mud remains without a satisfactory solution, and much improvement in the recycling of waste metal is needed. In 1970, approximately 3 billion aluminum beer- and soft-drink cans were made from 57,000 tons of aluminum. In that year, approximately 10 percent of the cans were recycled, and there was a modest increase the following year. Even if this marks the beginning of a trend, the problem of beer- and soft-drink-can litter control and disposal or reuse remains a monumental one.

GEOLOGIC ENVIRONMENT OF BAUXITE

Aluminum, surpassed in abundance only by oxygen and silicon in the crust of the earth, is a major constituent in many types of rocks. It occurs in nature only in combination with other elements—mostly with silicate minerals, the remainder with other compounds. Aluminum combined with oxygen and hydrogen makes up the minerals in bauxite deposits, and this is the form most commonly mined for metal. The principal minerals in bauxite are gibbsite, $Al(OH)_3$; boehmite, $AlO(OH)$; and diaspore, which has the same composition as boehmite but is denser and harder. Gibbsitic bauxites are designated the trihydrate type; boehmite- and diaspore-bearing bauxites are the monohydrate type. Trihydrate bauxites that have a low silica content (or low reactive-silica content) are the cheapest to process by the Bayer method. The extraction of alumina from monohydrate and mixed monohydrate-trihydrate bauxites is more costly because higher temperatures and pressures and additional amounts of caustic soda are required. Lower metallurgical costs make it possible to utilize trihydrate bauxite of lower grade than the other types.

Most of the bauxite deposits in the United States are composed chiefly of gibbsite; the principal impurity is kaolinite, $(OH)_8Si_4Al_4O_{10}$. Jamaican bauxite, the leading source of our imports, is chiefly gibbsite but also contains some boehmite. Most deposits in Europe and several in Asia are composed chiefly of boehmite. Minor quantities of diaspore are present in several bauxite deposits in foreign countries and occur in refractory-clay deposits in Missouri and Pennsylvania.

Bauxite minerals are formed mostly by weathering of aluminous rocks. Various deposits of bauxite in different parts of the world are known to have formed from virtually every type of rock that contains aluminum. Conditions favorable for the formation of bauxite are (1) warm tropical climate, (2) abundant rainfall, (3) aluminous parent rocks having high permeability and good subsurface drainage, and (4) long periods of tectonic stability that permit deep weathering and preservation of land surfaces. During weathering, the bauxite becomes enriched in aluminum by removal of most of the other elements in the parent rocks mainly by solution by subsurface water. Because of chemical weathering and removal of essential plant nutrients, soils developed on bauxite deposits commonly support a cover of undernourished, dwarfed vegetation.

Useful guides in exploration for surficial bauxite are the recognition of old land surfaces and dwarfed vegetation; such guides led to the discovery of the bauxite deposits in Oregon and Hawaii, as well as several very large deposits in other parts of the world.

Several types of bauxite deposits occur in the United States. The major deposits in the Arkansas region are of Eocene age, and they were formed by weathering of nepheline syenite (Gordon and others, 1958). Some deposits in this region are residual on the igneous rock; others have been transported and are interlayered with marine shale that was deposited in a sea that overlapped the syenite. The iron- and titanium-bearing low-grade bauxites (table 7) in Washington (Livingston, 1966), Oregon (Corcoran and Libbey, 1956), and Hawaii (Patterson, 1971) were formed from basalt lava flows. These deposits are of the laterite type and have origins similar to the very large deposits occurring in thick residual soils in several tropical areas. The deposits in Washington and Oregon occur on flows of probable middle Miocene age, and the bauxite is thought to have formed chiefly in late Miocene time. Those in Hawaii formed mainly during the Pleistocene Epoch. Some bauxite deposits in the Appalachian region occur in areas of karst topography, and apparently they formed by leaching of fine-grained aluminous materials that accumulated in sink holes. These deposits are thought to be early Tertiary in age.

TABLE 7.—*Chemical composition, in percent, of bauxite resources in the United States*

	Al_2O_3	SiO_2	Fe_2O_3	TiO_2	Loss on ignition
Arkansas	40–60	1–>20	3–>6	1–3	15–35
Oregon [1]	35.0	6.7	31.5	6.5	20.2
Washington [1]	38.8	6.6	28 7	4.2	21.7
Kauai, Hawaii [1]	25.9	4.7	39.4	6.7	20–23

[1] Average of several analyses.

RESOURCES

BAUXITE RESOURCES

Compared with world resources of metallurgical-grade bauxite, the United States reserves and potential resources are very limited. The domestic reserves, which are in beds 8 or more feet thick in Arkansas, amount to approximately 40 million tons. Potential resources of metallurgical bauxite in the laterite deposits in Hawaii, Washington, and Oregon, and thin, deeply buried deposits in Arkansas, amount to 250 to 300 million tons. Some of the deposits in Washington and Oregon are as rich in alumina as bauxite mined in some countries, but it has not been established that alumina can be extracted profitably from this bauxite. With the development of a process of profitable extraction, as much as 100 million tons could be shifted from conditional resources to the reserve category, thereby increasing the reserves to 140 million tons. But even with this larger figure, the United States would have only about 1 percent of the world's bauxite reserves.

World bauxite reserves were estimated in 1965 by Patterson (1967) to be 5.8 billion tons and potential resources to be 9.6 billion tons. Since this estimate was made, very large deposits have been discovered in several countries, and trihydrate bauxite containing as little as 35 percent Al_2O_3 is now mined in Australia and elsewhere. As the result of the use of lower grade bauxite, much of that considered to be potential resources in 1965 now should be classified as reserves. The total world bauxite reserves are now probably 12–15 billion tons. Lack of reliable data precludes estimating potential bauxite resources, but these resources are undoubtedly much larger than the 1965 estimate.

It is unlikely that new large deposits of metallurgical-grade bauxite will be discovered in the United States. Elsewhere, however, there are large unexplored areas in South America, Africa, Asia,

and Australia that seem favorable for discovery of major new deposits of metallurgical-grade bauxite.

Reserves of bauxite for abrasives, refractories, and chemicals in the United States are approximately 5 million tons, and potential resources are about 25 million tons. These deposits are in Arkansas (Gordon and others, 1958) and in many small districts scattered throughout the Appalachian region and the Coastal Plain in Southeastern United States (Overstreet, 1964). Chemical-grade bauxite is mined in Arkansas; Andersonville, Ga.; and the northwest Georgia districts. Refractory-grade bauxite is mined in Arkansas and in the districts at Eufaula, Ala., and Andersonville, Ga. Small quantities of refractory-grade bauxite are occasionally mined where lenses of bauxite are found during mining of kaolin in the extensive kaolin belt of Georgia. Much of the refractory-grade bauxite produced domestically is used for mullite-type refractory products because of its high silica content, and demand for such material is increasing. Abrasive-grade bauxite has been produced in the Arkansas district, but now most of it is imported in calcined form from Guyana and Surinam.

Guyana and Surinam are now the principal sources of high-grade refractory bauxite for most of the world. During the period of 1966–70, the United States imported yearly from 145,000 to 237,000 long tons of bauxite, mainly for uses other than metal, from Guyana (Kurtz, 1971, p. 6) and from 16,000 to 48,000 long tons from Surinam. Some calcined abrasive-grade bauxite has been recently imported from the Weipa district in Australia, and calcined bauxite is reported to be available in the Republic of Guinea; however, the long-range potential of these sources is not yet clear.

In the United States, possibilities remain for finding additional small deposits of bauxite for refractory and chemical uses in Arkansas and the Southeastern States. Such deposits are likely to be high in silica, and some will be deeply buried, but the search for these hypothetical deposits may become more profitable as domestic supplies diminish. Suggested areas for exploration are (1) beneath considerable cover downdip from the nepheline syenite body on which the Arkansas deposits were formed (Jespersen, 1964), and (2) in scattered areas in the southern Appalachian region, where sinkholes are abundant.

OTHER POTENTIAL RESOURCES OF ALUMINUM

Potential resources of aluminum other than bauxite comprise a variety of rocks and minerals, including alunite, aluminous shale and slate, aluminum phosphate rock, dawsonite, high-alumina clays, nepheline syenite, anorthosite, saprolite, coal ash, and aluminum-bearing copper-leach solutions. Alunite and nepheline syenite are being mined today in the U.S.S.R. for alumina and other products. Elsewhere in the world several of these resources have been investigated in considerable detail, but they are not mined because bauxite is available. The potential aluminum resources in the United States collectively amount to many billions of tons and are virtually inexhaustible. Their use will depend largely on costs of imported bauxite, alumina, and aluminum and on advances in technology that will make them competitive with imports. The United States could become self-sufficient in aluminum now if a profit in its production were not required.

ALUNITE

Alunite, $KAl_3(SO_4)_2(OH)_6$, a white mineral containing 37 percent alumina, commonly occurs in veins, replacement bodies, and in disseminated form in altered volcanic rocks. The mineral has potential value for potash and sulfur as well as aluminum. Alunite is a present source of aluminum in the U.S.S.R., and an alunite processing plant is reportedly under construction in Mexico. In the United States, alunite was investigated through the pilot-plant stage as an emergency source of aluminum during World War II.

Recently, alunite deposits near Cedar City, Beaver County, Utah, were explored by two companies (Engineering and Mining Journal, 1971). The deposits are on lands under Federal potash permits in the Wah Wah Mountains. Four zones of alunitized Tertiary volcanic rocks, each more than 100 million tons of rock, have been reportedly found by extensive drilling. The deposits are said to be 35–45 percent alunite, and the remainder is mostly quartz. Aluminum sulfate or alumina and potassium sulfate are the proposed products from this deposit (W. W. Walker, oral commun., May 1972). If this initial report on the size and grade of these deposits is confirmed, they are a large potential resource of aluminum, but whether or not this metal can be recovered profitably is yet to be determined.

ALUMINUM PHOSPHATE ROCK

The leached zone, 2–20 feet thick, occurring above and stripped off in mining of phosphate deposits in Florida, contains several aluminum phosphate minerals and minor quantities of uranium. The alumina content of this rock ranges from 4 to 20 percent, and the U_3O_8 content from 0.005 to 0.02 percent. These deposits in Florida extend over several hun-

dred square miles and were estimated to contain 800 million tons of this low-grade rock; however, part of this theoretical resource of alumina has been lost in mining.

Research has been carried on by industry and government organizations on the possibility of recovering alumina, uranium, and phosphate from these deposits and similar ones overseas. Some of the earlier efforts were sufficiently encouraging to generate the issuing of several U.S. and foreign patents, but no profitable extraction of aluminum has been achieved.

ALUMINOUS SHALE AND SLATE

Aluminous shale, containing 20–24 percent Al_2O_3, and slate, some of which is considerably richer in alumina, are widely distributed throughout the United States. The most extensive aluminous shale units were formed from fine-grained marine sediments. Those in Central and Eastern United States are of Paleozoic age, and those in the High Plains and Rocky Mountain regions are of Cretaceous age. Most slates in Eastern United States occur in a belt extending from Maine to North Carolina, and they are of Paleozoic age.

Shales have been investigated as possible sources of aluminum by several State agencies and by industry. The North American Coal Co. built a pilot plant at Powhatan Point, Ohio, and tested the shaly roof stone above the Pittsburgh coal bed. This attempt at commercial production was unsuccessful.

DAWSONITE

Dawsonite, $NaAl(OH)_2CO_3$, a colorless or white acid-soluble mineral, occurs in small needlelike crystalline aggregates or as fine-grained to microscopic crystals in several types of host rocks. Dawsonite contains, by weight, 35.4 percent Al_2O_3 or 18.7 percent aluminum metal. When heated it loses hydroxyl water and carbon dioxide and forms water-soluble sodium aluminate. Until its discovery in the Tertiary oil-shale deposits of Colorado, dawsonite was a mineralogical curiosity found only at a few localities in the world (Smith and Milton, 1966; Loughnan and See, 1967).

Large quantities of dawsonite and nahcolite (see discussion of nahcolite in chapter on "Evaporites and Brines") are present in the rich oil-shale deposits of the Tertiary Green River Formation in the Piceance Creek basin, northwestern Colorado. Dawsonite occurs as microscopic crystals disseminated throughout the oil shale in sequences as much as 1,000 feet thick toward the center of the basin. The top of the dawsonite- and nahcolite-bearing oil shale in the central part of the basin ranges from about 1,100 to 2,000 feet below the surface. The dawsonite content of the oil shale ranges from a few percent to at least 20 percent (Hite and Dyni, 1967). From an examination of well cuttings, DeVoto, Stevens, and Bloom (1970) identified a 500-foot-thick sequence of oil shale of potential commercial value in a 250-square-mile area in the northern part of the basin. The shale in this sequence contains a minimum of 1.5 percent acid-extractable aluminum (equivalent to 8 percent dawsonite), which amounts to a resource of about 19 billion short tons of equivalent dawsonite. In addition to the aluminum, the rock contains an average of about 30 gallons of shale oil per ton.

Alumina for production of aluminum metal and sodium aluminate for use in water-pollution control are potential products of dawsonite in the Colorado oil-shale deposits (Hite and Dyni, 1967; Irvin Neilsen, written commun., 1972). Recovery of either product seems most feasible after the rock has been retorted for shale oil. During retorting, the dawsonite would be converted to sodium aluminate which could then be extracted by a water or caustic leach (Dyni, 1972; VanNordstrand, 1968). Aluminum hydroxide could be precipitated from the sodium aluminate solution, then calcined to form alumina. Additions of nahcolite to the oil shale before retorting might improve the recovery of sodium aluminate (Hite, 1969). Although the amount of extractable aluminum is very low to serve as a commercial source of aluminum, the costs of mining and processing the rock would be partly offset by coproduction of shale oil and nahcolite (or soda ash) from the same rock. Furthermore, extraction of sodium aluminate from retorted dawsonite-bearing oil shale does not require the Bayer process which is necessary in processing bauxite for aluminum metal.

The dawsonite-bearing oil-shale deposits in Colorado originated in an ancient closed-basin lake environment whose waters were rich in organic matter and sodium carbonate. Vast amounts of carbonate minerals including dawsonite, nahcolite, and dolomite were precipitated from strongly alkaline solutions by mechanisms that are as yet unclear. Dawsonite seems to be restricted to the Piceance Creek basin; it has been looked for but not found in the Green River Formation in Utah or Wyoming. Elsewhere in the world small amounts of dawsonite have been found in dikes at Montreal, Canada, in sandstone from the Permian Greta Coal Measures in Australia, in alluvial claystones of Pleistocene age in Olduvai Gorge, Tanzania, and in a few other

localities of minor importance. Possibly, oil-shale deposits of lacustrine origin elsewhere in the world have potential for content of dawsonite and other sodium carbonate minerals.

HIGH-ALUMINA CLAYS

High-alumina clays consisting mainly of kaolinite have long been considered as a possible source of aluminum. During the World War II emergency, the possibilities for extracting alumina from such clays were evaluated in pilot plants at Salem, Ore., and Harleyville, S. C. Clays of this type were used as a source of aluminum in Germany and Japan during that war and have been investigated as a source of aluminum in Poland, the U.S.S.R., South Africa, and elsewhere in recent years. High-alumina clays have long been considered by the U.S. Geological Survey and the U.S. Bureau of Mines to be the most favorable potential source of aluminum from nonbauxite rocks in the United States, because of their high aluminum content and their availability. A panel of academic and industrial experts in liaison with government officials recently reaffirmed this position (National Materials Advisory Board, 1970, p. 1).

High-alumina kaolin and kaolinitic and refractory clays having alumina contents of 25–35 percent occur at many places in the United States (Patterson, 1967, p. 129–145; U.S. Bureau of Mines, 1967; chapter on "Clays"), mainly in sedimentary rocks of Pennsylvanian, Cretaceous, and Tertiary ages. Though the total resource of clays containing as much as 25 percent alumina is extremely large, the deposits that realistically can be considered to be major potential sources of aluminum are more limited. Those clays which are likely to be used for aluminum, if a breakthrough of the use of such materials is ever achieved, are likely to have rather restrictive characteristics; most particularly they will be high in grade, having average alumina contents of approximately 35 percent; and they will occur in very large deposits under geologic conditions permitting cheap strip mining and will be on lands owned by aluminum companies or on lands that can be acquired at a comparatively low cost. The principal limitation on the availability of high-alumina clay is that most of the large high-grade deposits under light overburden are now owned by companies producing various grades of kaolin and refractory and ceramic clays, and the value of these deposits for these uses is greater than for recovery of aluminum.

Areas where high-grade clay in quantities of 50 million tons are likely to be available include (1) deposits associated with bauxite in Arkansas; (2) the extensive Georgia kaolin belt; and (3) a belt of Eocene clay including the Andersonville district, Georgia, and extending northeast and southwest from that belt. The total amount of high-alumina clay in the United States containing 25 percent Al_2O_3 or more and under no limits of availability, overburden, or mining costs may be as much as 10 billion tons.

IGNEOUS ROCKS

Nepheline syenite and anorthosite are two igneous rocks that are potential sources of aluminum. Nepheline syenite is a medium- to coarse-grained soda-rich rock composed chiefly of nepheline, alkalic feldspars, and ferromagnesian minerals. In Arkansas, the alumina content of nepheline syenite ranges from 18 to 20 percent. Deposits of nepheline syenite occur in many other places in the United States and elsewhere in the world. A deposit of nepheline syenite in the Kola Peninsula, U.S.S.R., containing considerably more alumina than the Arkansas rock, has produced metal-grade alumina, fertilizer, fluorine, and cement for several years. A large new plant using similar rock in southern Siberia is also reported to be in production.

Anorthosite, a medium- to coarse-grained igneous rock, is composed mostly of plagioclase feldspar and contains 23–28 percent alumina. The rock forms large intrusive masses of Precambrian age near Laramie, Wyo., in California, in New York, and in many other localities in the United States and elsewhere in the world. A pilot plant operated in the early 1950's by the U.S. Bureau of Mines tested a method of recovering metal-grade alumina and cement from Wyoming. This work proved alumina can be recovered from the rock, but not at currently competitive costs. In the summer of 1972, the Aluminum Company of America announced the purchase of a large deposit of anorthosite in Wyoming.

Neither nepheline syenite nor anorthosite is likely to become a source of aluminum in the United States in the near future, although both constitute enormous low-grade resources amounting to billions of tons.

SAPROLITE

Saprolite is a rock whose original minerals are replaced by others during weathering but whose original textures and structures are preserved. The physical and chemical characteristics of these rocks are dependent on climate and drainage as well as the composition of the parent material. In the United States, saprolite deposits are extensive, amounting

to many millions of tons in the Piedmont region that extends from southern Virginia through the western parts of South Carolina and North Carolina, and northern Georgia and into northeastern Alabama. Little is known about the composition of these saprolite deposits. Analysis of a few samples collected near Shelby, N.C., and Gaffney, S.C., found the saprolite to contain 25–36 percent alumina, partly in gibbsite but much in very fine grained aluminum silicate minerals. Probably much of the silica in these rocks would be reactive and deleterious in alumina processing. Other large saprolite deposits are associated with the low-grade bauxites in Hawaii, Washington, and Oregon. Saprolite also occurs at several other localities in the United States.

Saprolite was investigated as a source of aluminum by several major aluminum companies during the 1950's. In 1970, large acreages were leased by a newly formed company to recover alumina from saprolite.

COAL ASH

Approximately 50 million tons of ash containing 8–40 percent alumina is produced by burning coal each year in the United States. Coal ash is an unlikely present-day source of aluminum because sufficient quantities are not generated in any one locality, and the ash may have been heated to temperatures that would make the alumina difficult to extract. As a long-range resource, however, coal ash may have some potential. If future energy requirements necessitate the use of large amounts of high-sulfur coal in steam-electric generating plants, possibly alumina and sulfuric acid could be recoverable byproducts.

COPPER-LEACH SOLUTIONS

Recent consideration has been given to recovering alumina from acid solutions used to leach copper from mine dumps and low-grade copper deposits in the United States (National Materials Advisory Board, 1970, p. 57–60). Repeated cycling of these solutions increases the alumina content; one copper company estimated that the amount of leach solution it circulated daily contains 1,000 tons of alumina. Potential resources of as much as 2,000 tons of alumina per day are estimated to be available from operations of 14 copper mines in the United States.

PROBLEMS FOR RESEARCH

On the assumption of a politically stable period in the world, it seems likely that the growing demand in the future for aluminum in the United States will be met largely by imports. It is anticipated that the current trend of increasing imports of alumina and aluminum, rather than of bauxite, will continue. This condition could change if methods are developed for economic recovery of aluminum and coproducts from nonbauxite domestic sources. High-alumina clay, dawsonite-bearing oil shale, and possibly alunite seem to be the most promising nonbauxite domestic sources of aluminum.

Continued research on the geology of bauxite deposits of the world is needed. This research should include exploration for additional major deposits, particularly in tropical areas, as well as continued investigations of the size, depth, thickness, grade, composition, impurities, and possible byproducts of known foreign deposits.

New tools and methods to aid in prospecting and in the evaluation of bauxite deposits would indeed be useful. In the past, in the evaluation of deposits no substitute has been found for detailed augering or drilling and the analyzing of numerous samples. A breakthrough in expediting the analytical workload may have come recently when one company introduced a modern semimobile laboratory in the Amazon Basin bauxite region (Mining Engineering, 1971). This laboratory is reported to have an atomic-absorption spectrophotometer, photoelectric colorimeter, and a rotating heat-pressure digestion system. Another major aid in exploration may result from a neutron-activation probe developed by Allan B. Tanner, Robert M. Moxham, and Frank E. Senftle of the U.S. Geological Survey and J. A. Baicker of the Princeton Gamma Tech Corporation (Tanner and others, 1972). This probe, when lowered down a drill hole, will provide semiquantitative determinations of the aluminum in the wallrock. Information on the content of titanium, iron, and other possible metallic byproducts in the bauxite might also be obtained by this method.

Additional research and information are needed on domestic potential sources of aluminum and on the location, size, grade, and principal mineral and impurity contents in several high-alumina clay deposits. Detailed studies of the geology, mining, and metallurgy of the dawsonite-bearing oil-shale deposits in Colorado by the U.S. Geological Survey and the U.S. Bureau of Mines are continuing. If the reported large deposit of alunite in Utah is confirmed, geologic studies of this deposit and similar ones in the Western United States would be warranted. Much information related to costs of extracting alumina from non-bauxite materials is also

needed. This need is emphasized by the recommendation of the National Materials Advisory Board (1970, p. 1) that the U.S. Bureau of Mines, with financial help and cooperation of the aluminum producers, should select the best acid process for recovering aluminum from clay and build and operate an alumina plant to provide information on costs.

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ANTIMONY

By M. H. Miller

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ABSTRACT OF CONCLUSIONS

The United States consumes each year about 40 percent of the world's supply of primary antimony. Deposits in this country furnish only about 15 percent of the antimony consumed, and most of this is recovered as a byproduct from silver, copper, and lead-zinc ores, mainly in Idaho, and as antimonial lead from lead smelters; most of the antimony used is imported from the Republic of South Africa, Mexico, and Bolivia. Identified resources in the United States, here estimated to be 100,000 short tons, are in Western States, mainly Idaho, Nevada, Alaska, and Montana; principal identified world resources, estimated at 5,600,000 short tons, are in China, Bolivia, the U.S.S.R., Republic of South Africa, and Mexico. Future antimony resources may be developed from Mississippi Valley-type lead deposits and from certain base-metal deposits in the Eastern United States. The possibility of future production from these sources will hinge on the ability of lead smelters to continue operations and meet standards set to protect the environment.

INTRODUCTION

Antimony is a brittle silver-white metal that has a specific gravity of 6.6 and a melting point of 630.5°C. It imparts strength, hardness, and corrosive resistance to alloys.

Antimony is marketed as metal, oxide, antimonial lead, and sulfide. Metallic antimony is sold under brand names; each brand name commonly represents metal with a guaranteed antimony content, and an allowable maximum content of arsenic and other minor constituents detrimental to many uses of antimony.

The largest use of antimony in the United States is in the manufacture of storage batteries. Automobile batteries contain as much as 12 percent antimony, but most manufacturers now are using 4–6 percent antimony alloyed with lead. Very high purity antimony metal (99.999+ percent pure) is used in intermetallic compounds for semiconductors and other chemical applications. Antimony is used as a hardening agent in metals used in chemical pumps, tank linings, roofing sheets, plumbing fixtures and pipes, cable sheaths, foil, and bullets. Antifriction bearings, type metal, solder, and decorative castings of Britannia metal and pewter also contain antimony. "Antimony black" is finely divided metallic antimony used in bronzing for metals and plaster casts.

Antimony oxides are used in paints and plastics as a pigment and fire-retarding agent and in white ceramic enamels as an opacifying agent. With suitable stabilizers and coloring additives, antimony trioxide glass can be made opaque to all visible light except long-wave infrared rays.

Antimony sulfides are used in the manufacture of ammunition primers, smoke generators, visual

range-finding shells, tracer bullets, and fireworks and as a vulcanizing agent in the rubber industry. A small amount of antimony sulfide is also used in friction matches.

Organic antimony compounds are used in the treatment of certain parasitic diseases. Potassium antimonyl tartrate has been used as a nauseant and expectorant.

U.S. consumption of primary antimony was about 23 percent lower in 1970–71 than during the previous 4-year period. This may reflect consumer resistance to the high price level during 1970, but antimony prices in June 1971 were comparable to October-November 1969 prices, and prices continued the downtrend during the last half of 1971. More than 80 percent of the U.S. smelter output of primary antimony is derived from imported antimony ores and concentrates or byproduct antimony from foreign lead ores; domestic antimony ores account for about 7 percent and byproduct antimony from lead-silver ores accounts for 9 percent of the antimony produced.

Other substances may be substituted for antimony in most uses, but substitutes may be in short supply or may be more expensive to use. Substitution is restricted by the necessity of making changes in production techniques and factory equipment. Mercury, titanium, lead, zinc, chromium, tin, and zirconium may substitute for antimony in paints, pigments, and enamels. Possible substitutes for antimony-hardened lead are tin, calcium, and dispersion-hardened lead; selected organic compounds have been accepted as alternative materials in flameproofing.

Antimony is a strategic commodity because of its important military uses. Concern about future supply of antimony is increased by the dependency of the United States on imported ores and concentrates. The United States receives about 50 percent of its imported antimony ores from the Republic of South Africa; Mexico and Bolivia, important suppliers in the past, still account for about half the ore imports.

EXPLOITATION

Stibnite deposits and occurrences were discovered in Nevada as early as the 1860's, and some antimony ore was produced as early as 1865. Idaho's production started in the early 1890's.

Military importance of antimony was first realized during World War I; the shortage resulting from military uses was eased to some extent by increased domestic production and imports from Bolivia. The price for antimony dropped from a high of 45 cents per pound in 1916 to a low of 4 cents per pound in 1922. Expanded use of storage batteries in the automobile industry increased antimony consumption during the 1930's. (See fig. 8.) World War II escalated the demand for antimony, and idle domestic mines were reopened and foreign mines expanded production. Secondary antimony recovered from scrap became a major supply source.

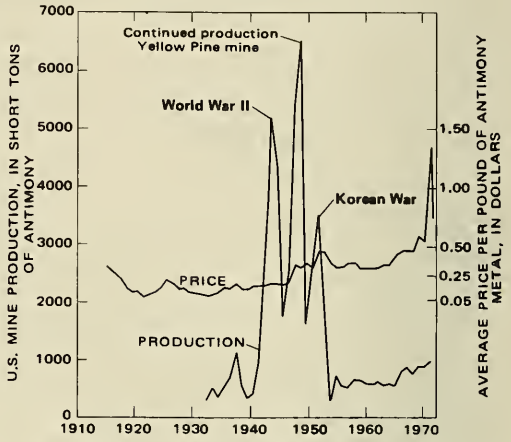

FIGURE 8.—Price and production of antimony in the United States, 1916–70.

World War II antimony production peaked in 1943 when U.S. mines produced 5,111 short tons of contained antimony, largely from the Yellow Pine mine of Idaho. Production peaked again in 1948 at the all-time high total from U.S. mines of 6,489 short tons of contained antimony, again largely from the Yellow Pine mine. This production peak reflects the continued production of antimony at the Yellow Pine mine after the high-grade tungsten-antimony ore was exhausted. In 1951, domestic production attained a minor peak of 3,472 short tons of contained antimony, probably paralleling increased military needs during the Korean War. Thus, the three production peaks occurred during one 10-year period, 1942–52.

The price for imported antimony metal, at New York, reached a high of $4 per pound early in 1970, and the price for imported ore and concentrates, 60 percent antimony, topped at $43–$45 per long-ton unit in June 1970. Peak prices of RMM ($1.76 per lb) and Lone Star ($1.77 per lb) metals produced by NL Industries, Inc., at Laredo, Tex., were reached in April 1970, and they held at that level through August 1970. Production from mines in the United

States rose from 938 short tons of contained antimony in 1969 to 1,130 short tons in 1970 and then dipped to 992 short tons in 1971. In 1969, U.S. smelter production was 13,203 short tons of contained antimony as compared to 13,381 short tons in 1970 and 13,157 short tons in 1971. These statistics indicate that the amount of antimony mined in the United States and that produced by U.S. smelters are not greatly affected by price fluctuations. Mines reopened primarily for antimony could not reach a production stage soon enough to take advantage of the higher prices. Price levels during the first quarter of 1972 approximated those of the third quarter of 1969.

Although antimony is toxic when taken internally, its production alone probably would not constitute a hazard to the environment. Lead smelters, where antimonial lead is recovered, may be detrimental to the environment, and many smelters cannot meet present-day emission standards.

GEOLOGIC ENVIRONMENT

GEOCHEMISTRY

The abundance of antimony in the earth's crust ranges from 0.2 to 0.5 ppm (parts per million). In igneous rocks the abundance is 0.1–1 ppm. According to Vinogradov (1962), basalts contain the highest percentage of antimony, and Turekian and Wedepohl (1961) found that deep-sea clays contain 1 ppm antimony.

The chemical and physical properties of antimony are similar to those of arsenic and bismuth. Antimony is chalcophile in distribution and combines readily with sulfur and the preferred heavy metals lead, copper, and silver. Metallic minerals found in association with primary antimony minerals are pyrite, galena, sphalerite, chalcopyrite, arsenopyrite, pyrrhotite, gold, and silver; the common gangue minerals are quartz (predominantly), calcite, and barite.

The amount of antimony found distributed through sedimentary rocks is very small, and the changes that anitmony undergoes in the weathering process are obscure. Antimony, like arsenic, tends to be concentrated in hydrolyzates, chiefly by adsorption on ferric hydroxide. Although the antimony content of sea water is beyond limits of detection by most analytical methods, small amounts have been reported in some marine animals and in ashes of seaweeds. Although data are lacking, it seems likely that during metamorphism much antimony in stibnite is quickly remobilized and moved through and into fissures, fractures, and brecciated zones, again forming low-temperature hydrothermal deposits.

MINERALOGY

Stibnite, Sb_2S_3, is the predominant ore of antimony; next in importance are valentinite, Sb_2O_3; senarmontite, Sb_2O_3; stibiconite, $Sb_2O_4 \cdot H_2O$; bindheimite, $Pb_2Sb_2O_7 \cdot nH_2O$; and kermesite, $2Sb_2S_3 \cdot Sb_2O_3$. Tetrahedrite, $Cu_8Sb_2S_7$, has become an important antimony ore, and jamesonite, $Pb_2Sb_2S_5$, has been mined from deposits at Zimapán, Hidalgo, Mexico; Candelaria, Nev.; and the Arabia district, Nevada.

TYPES OF DEPOSITS

Antimony occurs in a variety of deposits—epithermal veins, pegmatites, and replacement and hot-spring deposits. Deposits of antimony range in age from Precambrian to Quaternary. Wang (1952, p. 6–10) showed a rather complex classification of worldwide antimony deposits; White (1951; 1962) classified world deposits into two types, with gradations between these types; one of these is mineralogically and structurally simple and the other complex.

Simple antimony deposits consist principally of stibnite, or rarely, native antimony in a siliceous gangue, commonly with some pyrite and in places a little gold and small amounts of other metal sulfides, principally silver and mercury. The "manto" deposits of Mexico are of the simple type and consist of selective replacements of favorable limestone beds, generally overlain by shale. Most stibnite of the hypogene deposits is oxidized to one or more of the antimony oxides. Most deposits of Mexico, Bolivia, Peru, China, Republic of South Africa, Yugoslavia, Algeria, Hungary, Czechoslovakia, Italy, and Japan are of the simple type.

Complex antimony deposits consist of stibnite associated with pyrite, arsenopyrite, cinnabar, or scheelite or of antimony sulfosalts with varying amounts of copper, lead, and silver as well as the common sulfides of these metals and zinc. Ores of the complex deposits generally are mined primarily for lead, gold, silver, zinc, or tungsten. Most of the antimony produced in the United States, Australia, and Canada is from complex deposits.

Neither the simple antimony deposits nor the complex ones can be said to have affinity for a specific rock type, U.S. deposits range in age from Precambrian to Tertiary (White, 1962). Although many U.S. deposits are of Tertiary age, equally as many are of Mesozoic age, and about one-fifth of the deposits are of Paleozoic age. Deposits closely asso-

ciated with Mesozoic or Tertiary igneous rocks are about equally divided between dikes and lava flows and coarse-grained intrusive rocks, commonly granodiorite or quartz monzonite. The often-held view that antimony deposits are of Tertiary age and volcanic association is an oversimplification.

Most antimony produced in the United States comes from the complex deposits, as a byproduct of the treatment of silver, lead, copper, and zinc ores. The deposits in the Coeur d'Alene district, Idaho, are outstanding examples of complex deposits. In the Yellow Pine district, Valley County, Idaho, another example of an area of complex ores, gold and tungsten were the principal metals, but with a high enough price antimony outvalues the other metals. For detailed information about specific U.S. deposits, see White (1951; 1962).

Most antimony deposits presumably formed from hydrothermal solutions at relatively low temperature and shallow depth, which gave rise to filled fissures, joints, and irregular replacement masses. In places, antimony is disseminated through the wallrock alteration zone.

RESOURCES

IDENTIFIED AND HYPOTHETICAL RESOURCES

Estimated identified and hypothetical resources are summarized in table 8; these estimates are based on sparse data in files of the U.S. Geological Survey and a few published sources of information on the occurrence of antimony as a relatively minor constituent in ore deposits of major metals. Approximately 25 percent of the known U.S. antimony resources is in scattered simple-type deposits, which are not of economic importance unless the price for ore or concentrates would triple or quadruple and stabilize at that level. Although 25 percent of the U.S. antimony resources is contained in the Yellow Pine district, little antimony has been produced since the Yellow Pine mine was closed in 1952. Ranchers Exploration and Development Corporation leased the Yellow Pine mine and carried out a diamond-drilling program in 1970, but there is no indication that any ore was produced (B. F. Leonard, oral commun., 1972). At least 50 percent of the U.S. antimony resources is contained in known complex lead-silver-copper and gold ores.

TABLE 8.—*Estimated world resources of antimony, in short tons of metal*

[Figures are modified from data compiled by U.S. Bureau of Mines except where otherwise noted]

Country	Identified resources [1]	Hypothetical resources [2]
United States	100,000	[3] 100,000
Mexico	200,000	
Bolivia	420,000	
Yugoslavia	100,000	
Turkey	120,000	
Republic of South Africa	300,000	
U.S.S.R.	300,000	
China	3,800,000	1,500,000
Thailand	110,000	
Australia	150,000	
World total	5,600,000	

[1] Identified resources: Specific, identified mineral deposits that may or may not be evaluated as to extent and grade and whose contained minerals may or may not be profitably recoverable with existing technology and economic conditions

[2] Hypothetical resources: Undiscovered mineral deposits, whether of recoverable or subeconomic grade, that are geologically predictable as existing in known districts.

[3] Based on unpublished data in files of U.S. Geological Survey.

During the last 40 years, about four-fifths of U.S. mine production of antimony has come from Idaho. Reserves of ore in the Coeur d'Alene district are considered adquate for continuous operations for many years.

The Fairbanks district, Alaska, has produced about 2,500 tons of stibnite ore, and since 1936, when it began operations, the Stampede mine in the Kantishna district, Alaska, has produced about 2,700 tons of stibnite ore. About 75 percent of Alaska's antimony was produced before World War II. From 1960 to 1971, about 100 tons of antimony was produced from Alaskan deposits, mainly the Stampede mine. Known Alaskan resources are estimated as nearly 10,000 tons of low-grade material (Berg and others, 1964).

On the basis of scattered analyses, it is estimated that lead ores in southeastern Missouri, the Tri-State district, and the Upper Mississippi Valley may contain as much as 50,000 tons of antimony, here considered as a hypothetical resource. So far as is known, no antimony is now being recovered from these ores.

SPECULATIVE RESOURCES

Potential resources of antimony that may be mined in the future are tied directly to lead-silver-copper-zinc deposits like those from which most domestic antimony is recovered as a byproduct or coproduct.

Antimony is present in some galenas from Mississippi Valley-type lead deposits (Allen Heyl, oral commun., 1972), and antimony is a constituent of some base-metal deposits in the Eastern United States. Apparently, fringe areas of some mineralized zones, such as in Nevada, show anomalous amounts of antimony; potential resources possibly exist there. When the United States can no longer import antimony in quantities to meet the needs, some additional domestic production may be obtainable from these base-metal deposits and from areas of known base-metal, tungsten, silver, and gold mineralization.

PROSPECTING TECHNIQUES

Historically, very little prospecting has been directed solely toward antimony; probably most was incidental to prospecting for gold, silver, lead, or copper. In some instances, although antimony was not detected in sulfides or oxides of certain metal deposits, antimony has been recovered during smelting of the ores. Where antimony is recognized, prospectors have searched successfully for extensions of known deposits and for other deposits in or near known occurrences.

Geochemical methods of determining antimony in soils and rocks have been tested in the laboratory and under field conditions (Ward and Lakin, 1954; Jardine, 1963; Ward and others, 1963). The field method described by Ward and Lakin (1954) was used successfully by Sainsbury (1957) in geochemical exploration for antimony in Alaska.

PROBLEMS FOR RESEARCH

Detailed geologic studies of the occurrence of antimony-bearing minerals in known deposits, especially those minerals in which antimony substitutes for another element, would broaden our base of knowledge and enhance the possibility of delineating areas that contain additional antimony resources.

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ARSENIC

By J. L. Gualtieri

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ABSTRACT OF CONCLUSIONS

Arsenic is used mostly in agriculture, where it is employed as an insecticide, pesticide, and herbicide. It has limited use in industry as an alloying agent and a chemical reagent.

Current domestic consumption of arsenic is about 20,000–30,000 short tons per year, but domestic production fills only about a tenth of this. The rest is mostly supplied by other countries of the free world, chiefly Sweden, France, and Mexico.

Arsenic is produced as a byproduct and occurs in several types of deposits: enargite-bearing copper-zinc-lead deposits, arsenical pyritic copper deposits, native silver and nickel-cobalt arsenide deposits, arsenical gold deposits, arsenic sulfide and arsenic sulfide gold deposits, and arsenical tin deposits.

U.S. and world identified resources of arsenic are herein estimated to be 1,300,000 short tons and 17,600,000 short tons, respectively; these resources are more than sufficient to fill projected needs until the year 2000. Hypothetical resources for the United States and the world are estimated at 650,000 short tons and 14,300,000 short tons, respectively.

Speculative resources of arsenic are estimated to be 10 million short tons. Arsenic may be obtainable from organic shale of marine origin; where such shale is subjected to tectonic and metamorphic processes, contained metals may migrate to and concentrate in favorable structures.

INTRODUCTION

Elemental arsenic in its most stable form is a silver-gray metalloid, moderately hard but brittle and having a specific gravity of about 5.73. It rarely occurs naturally in its native state.

Arsenic is chemically allied to a group of elements which includes nitrogen, phosphorus, antimony, and bismuth; but it is physically more like antimony and bismuth, which also have metallike qualities.

Arsenic is important because of its toxic effect on living matter; its principal use is in agriculture where arsenic compounds function as insecticides, pesticides, and herbicides. Arsenic acid is used as a defoliant or dessicator to facilitate the mechanical harvesting of cotton. Organic arsenic compounds are used to control or to kill undesirable grasses and as parasite control agents in poultry and livestock. Other arsenic compounds are used as wood preservatives.

Uses of arsenic in industry are minor compared with those in agriculture. Arsenic is used as a decolorizer in the manufacture of glass, and arsenic compounds are used as pigments in some enamels and as reagents in flotation processes for separating minerals.

Metallurgically, arsenic is used as a hardener for lead in bearing metal, battery plates, and shot. It is

also alloyed with copper to give increased corrosion and erosion resistance and a higher annealing temperature.

Potential uses of arsenic include the manufacture of gallium arsenide or gallium arsenide phosphate diodes, improved lead-antimony or lead-tin-antimony alloys, catalysts used in the formation of some organic compounds, and nucleating agents in ceramic manufacture. The potential uses of the element, however, are not expected to increase its consumption appreciably.

Arsenic and arsenic compounds are important to the production of certain crops in countries that have developed advanced agricultural technologies—the United States, Canada, the countries of western Europe, Australia, and New Zealand, and to a lesser degree, the U.S.S.R. and the countries of eastern Europe. Industrial-technological-scientific societies have developed only where manpower has been freed from the production of foods and textiles. The initial increases in agricultural productivity resulted from mechanization; later increases resulted from the use of chemical fertilizers and improved seed; and more recent increases resulted from the use of insecticides, pesticides, and herbicides. Insecticides, pesticides, and herbicides play an important role in achieving the standard of living now enjoyed by the advanced nations, and they undoubtedly will play an increasing role in advancing the standard of living of the emerging nations.

Substitutes have been sought for arsenic compounds, not because arsenic is in short supply or is exepnsive, but because it is toxic to humans. In place of inorganic arsenic compounds, a group of chlorinated hydrocarbons and organic phosphorous compounds have been developed which are claimed to have lower toxicities for humans. Substitutes for arsenic used in industrial and metallurgical processes may in part be met by the chemically allied metalloids antimony and bismuth.

Domestic consumption of arsenic fluctuates from about 20,000 to about 30,000 short tons per year. An estimate for 1968 shows that the United States consumed or stocked the equivalent of 26,200 short tons of arsenic. Of this amount, 2,900 tons (11 percent) came from domestic sources and 23,300 tons (89 percent) came from foreign sources, either in arsenic metal and compounds or in ores and concentrates. Of the imports, Sweden supplied 37 percent, Mexico 28 percent, and France 26 percent. Only about 40 tons (about 0.2 percent) came from the Communist world, although in 1967 shipments from this source exceeded 1,000 tons.

The domestic output of arsenic is insufficient to meet current demand, although the United States has both the sufficient arsenic resources and the production facilities to meet demand. The increasing reliance on foreign sources, which has taken place over the last 25 years, is chiefly due to economics.

EXPLOITATION

Arsenic, because it is recovered as a byproduct, has had a history of exploitation different from that of most other commodities. It is removed from various ores during smelting, but its output is dependent upon several factors, including size, grade, and type of deposits, availability of smelter facilities, and price policies at custom smelters. Arsenic-rich segregates are refined at smelters with facilities for doing so. Where facilities are lacking or are idle, the segregates are stockpiled and shipped to other processing plants. Supplies have normally exceeded requirements and can be increased when necessary by activiating idle processing plants to recover arsenic from ores not ordinarily so treated.

Significant arsenic production started around 1900 and has increased steadily since then. Arsenic first was produced from arsenical gold deposits and later from other types of deposits. The arsenic-rich Boliden cooper deposit in Sweden started producing in 1926 and in large part made Sweden the world's foremost producer of arsenic.

Environmental problems resulting from exploitation of arsenic-bearing deposits are similar to those of other deposits. Access roads, mining, milling, and smelting and the disposal of overburden material, waste rock, mill tailings, and slag all tend to disturb the original environment of any area. At best these disturbances can only be minimized, and then at some cost. With the final cessation of mining and allied activity, some operational areas can be restored to approximate original conditions but at considerable cost.

Where arsenic in sulfide minerals is exposed to the atmosphere, as in the waste dumps of mines, soluble arsenates may be formed which can be a source of stream pollution. Smelters which treat arsenical sulfide ores can lose arsenic to the atmosphere in the form of arsenic oxides or arsine, AsH_3, although most of the arsenic volatilized in smelting and roasting forms a fine ash or dust which is arrested in the smelter stacks or Cottrell precipitators.

GEOLOGIC ENVIRONMENT

GEOCHEMISTRY

Arsenic is a relatively rare crustal element, con-

stituting about 2 ppm (parts per million) of igneous rocks (Onishi and Sandell, 1955) but 60 ppm or more of magmatic sulfide minerals (Rankama and Sahama, 1950, p. 739). Geochemically, arsenic is similar to antimony and bismuth. All three elements combine with sulfur, selenium, and tellurium. They form sulfosalts, arsenides, and antimonides with various heavy metals and show a preference for combining with copper, iron, nickel, and cobalt.

Some sulfide ores contain varying amounts of arsenic, antimony, and bismuth. Research on the mineralogy of these elements is incomplete; their presence has been established only in galena.

Arsenic occurs sparingly in the early and main stages of magmatic crystallization. Early magnetite and hematite contain little arsenic, and although the early magmatic sulfide minerals contain relatively large amounts, the late magmatic sulfides are strongly enriched. Arsenic first occurs as a distinct mineral (arsenopyrite) during the pegmatitic stage, but in most minerals it develops in the pyrometasomatic and hydrothermal stages of magmatism.

Arsenic tends to precipitate in extremely fine grained sedimentary materials that are made up of chemically undecomposed comminuted rock and insoluble rock residues derived through hydrolytic decomposition. It is especially concentrated in sediments that contain relatively large quantities of iron and manganese oxides, principally by adsorption on ferric hydroxide. Whereas as little as 4 ppm arsenic is found in bottom sediments of the Atlantic Ocean, as much as 65–650 ppm is found in ancient sedimentary iron ores. It is driven from iron-rich sediments through metamorphic processes. Arsenic is also precipitated with pyrite that was formed in carbonaceous oozes. More than 3,000 ppm of arsenic is reported in sedimentary pyrite.

Arsenic forms the anion AsO_4, which is isomorphous with the anion PO_4; consequently, arsenates substitute for phosphates and are present in both marine organisms and phosphate deposits. A small part of the arsenic in marine environments, however, escapes precipitation and remains in solution, possibly as an arsenite.

MINERALS

Arsenic occurs in more than two dozen minerals, but only a few are commonly found in ore deposits. The primary arsenic minerals are arsenopyrite ($FeAsS$), löllingite ($FeAs_2$), smaltite ($CoAs_2$), chloanthite ($NiAs_2$), niccolite ($NiAs$), tennantite ($Cu_3As_2S_7$), enargite (Cu_3AsS_4), and proustite (Ag_3AsS_3).

The supergene arsenic minerals are arsenolite (As_2O_3), mimetite ($PbCl \cdot Pb_4As_3O_{12}$), olivenite ($Cu_3As_2O_8 \cdot Cu(OH)_2$), realgar ($AsS$), orpiment ($As_2O_3$), scorodite ($FeAsO_4 \cdot 2H_2O$), and pearceite ($Ag_9AsS_6$).

TYPES OF DEPOSITS

No ore deposit is currently being mined solely for arsenic, although in the past, a few deposits high in arsenic were so mined for brief periods. Arsenic occurs in various types of metalliferous deposits which are classed in their approximate order of importance on the basis of estimated past production. They are as follows:

1. Enargite-bearing copper-zinc-lead deposits
2. Arsenical pyritic copper deposits
3. Native silver and nickel-cobalt arsenide deposits
4. Arsenical gold deposits
5. Arsenic sulfide and arsenic sulfide gold deposits
6. Arsenical tin deposits
7. Other deposits

ENARGITE-BEARING COPPER-ZINC-LEAD DEPOSITS

Enargite-bearing copper-zinc-lead deposits occur almost exclusively in orogenic belts in areas characterized either by granitic bodies or by volcanic rocks including vent deposits and mafic dikes and sills. Host rocks, in addition to granitic and volcanic rocks, include metasedimentary rocks of clastic origin and rarely carbonate rocks.

Enargite-bearing copper-zinc-lead deposits have complex mineralogies. This is due in part to repetitive episodes of dissimilar mineralization, in part to supergene alteration, and in part to the location of some deposits in extremely arid climates where otherwise soluble minerals are stable.

The more important minerals characteristic of the ores are enargite-famatinite, tetrahedrite, and pyrite, with quartz gangue; enargite-famatinite with native bismuth, argentian galena-sphalerite, tetrahedrite, pyrargyrite, and stephanite, with pyrite gangue; pyrite, enargite, tennantite, bornite, chalcocite, sphalerite, and a little chalcopyrite and covellite; and pyrite, chalcopyrite, sphalerite, galena, and lesser amounts of tetrahedrite and enargite. Supergene chalcocite is important in those deposits where near-surface copper was oxidized, leached, and redeposited at depth. In the oxidized zones of some deposits, native silver is important.

Enargite is the only important arsenic-bearing mineral; arsenolite and scorodite are present in the oxidized zone of some deposits but are sparse.

The deposits occur in veins and in massive blanket or lensoidal bodies. Vein deposits occur in sets of fractures or faults; some of the faults were active

during mineralization. The evins may be hundreds to thousands of feet long, as much as several tens of feet thick, and widely spaced, or they may be relatively short, thin, and closely spaced. The veins are commonly curvilinear and from place to place change in strike and dip; some veins split to form one or more additional veins.

The massive deposits occur in lenticular bodies measuring hundreds to thousands of feet in width and length and as much as 200 feet thick; they conform to controlling structures such as bedding and to the contacts between rock units. The vein deposits are structurally controlled, although most occur in granitic rock. They are in multiple sets of small faults or fractures, some of which may have been guided along a preexisting structural grain. Preferred mineralization of one set of fractures or faults over another may be due to availability of openings during the mineralization process.

Some massive bodies measuring hundreds of feet in length and width occur along or associated with major faults. The Cerro de Pasco deposit of Peru is located along a thrust fault of regional extent, but the significance of the fault as a controlling factor is unknown. The upper plate is mineralized and encloses manto-type sulfide deposits.

Enargite-bearing copper-zinc-lead deposits are among the largest ore deposits known. The deposit at Butte, Mont. (Meyer and others, 1968, p. 1395–1403), from 1880 to 1964 produced 318,234,680 pounds of arsenic compounds, although arsenic was not recovered during all this period. The tenor of mined copper over this period was about 2½ percent; that of arsenic is estimated to have been about 0.1 percent. Some of the other deposits of this type are, or will be when fully developed, comparable in size and tenor.

Other important deposits are Chuquicamata, Chile (Taylor, 1935, p. 473–484), Cerro de Pasco (McLaughlin and others, 1935, p. 517–527) and Morococha, Peru (Graton and others, 1935, p. 528–544), and Lepanto, Republic of the Philippines (Kinkel and others, 1956).

Enargite-bearing vein deposits are generally thought to be hydrothermal in origin and to have been derived from adjacent granitic plutons.

The massive deposits were long considered to be sedimentary-syngenetic veins or lodes that were deposited by ascending solutions or by hydrothermal replacement of crushed or sheared zones. More recently, they have been considered to be of volcanic-syngenetic origin and to have been produced by base-metal-rich sulfide emanations emitted during submarine volcanism (Anderson, 1969).

ARSENICAL PYRITIC COPPER DEPOSITS

Arsenical pyritic copper deposits occur in Precambrian terranes associated with metasedimentary and metavolcanic rocks, in Precambrian magmatic granite, and in orogenic belts with carbonate rock. Host rocks include rhyolite or tuffaceous schist, biotite schist, chlorite or chlorite-sericite schist, andalusite, sericite schist, conglomerate, calcareous breccia, and limestone.

The metallic minerals include pyrite, chalcopyrite, pyrrhotite, arsenopyrite, sphalerite, galena, pyrargyrite, tetrahedrite or tennantite, and native gold; gangue minerals include quartz, tourmaline, dolomite, ankerite, and sericite. Bismuth minerals are present in some deposits. Arsenopyrite and tennantite are the only arsenic-bearing minerals; arsenopyrite occurs sparingly or abundantly and is either evenly distributed or concentrated in nodular masses; tennantite, although more evenly distributed in deposits in which it is present, is very minor.

Arsenical pyritic copper deposits occur in massive tabular or lenticular bodies as much as several hundreds of feet long and at least 100 feet thick, or in pipelike masses several hundred feet in diameter and thousands of feet in vertical extent. Some deposits of this type seem to be controlled by steeply dipping shear zones or drag folds. They also occur consistently at or near the contacts of rock units. Deposits in foliated rocks follow the grain of the schistosity, a feature preserved in the ore; fractured or brecciated textures that were formed during mineralization are also displayed in the ore.

The size of the deposits ranges from a few hundreds of tons to millions of tons. The Boliden mine of Sweden, now exhausted, produced 8,341,550 metric tons of ore which contained 556,000 metric tons (620,000 short tons) of arsenic, an average of 6.91 percent, in addition to 1.42 percent copper, 15.2 grams per metric ton of gold, and 49 grams per metric ton of silver. Other deposits of this type which contained more copper (5–6 percent) contained only a fraction of 1 percent arsenic.

In addition to the Boliden deposit (Grip and Wirstam, 1970), examples of this type include the Rammelsberg deposits in the Federal Republic of Germany (Lindgren and Irving, 1911), the United Verde mine in the Jerome area of Arizona (Lindgren, 1926, p. 32–35, 61–78; Anderson and Creasey, 1958, p. 92), and several deposits on the island of Honshu, Japan (Kanehara, 1935, p. 688).

Arsenical pyritic copper deposits have been considered epigenetic and to have formed by replacement; those in schistose rock, for example, display relic foliation inherited from the host. The miner-

alizing solutions were thought to be hypothermal, although no deposit could be traced with certainty to a magmatic source. More recently, the supracrustal host rocks appear to be the source of the metals; the metals, mobilized by deep-level granitization, moved ahead of a migmatite front to accrete in favorable host structures or strata (Grip, 1960, p. 3–14). A volcanic-syngenetic origin also has been suggested for deposits of this type.

NATIVE SILVER AND NICKEL-COBALT ARSENIDE DEPOSITS

Deposits containing native silver and arsenides of nickel and cobalt are numerous in Precambrian shield areas and in orogenic belts. In shield areas the deposits are associated with belts of volcanic and related intrusive rocks and with sedimentary rocks derived from volcanic rocks, whereas in orogenic belts the deposits appear to be associated with small igneous bodies that were intruded into a variety of sedimentary rocks. The host rocks are diabase, mafic and intermediate lavas, conglomerate, graywacke, quartzite, and metamorphosed and granitized sedimentary rocks.

The major metallic minerals in these deposits are native silver, argentite, chalcopyrite, galena, pyrite, pyrrhotite, sphalerite, tetrahedrite, and native bismuth, accompanied by lesser amounts of proustite, pentlandite, polybasite, stephanite, and stromeyerite. Collectively important is the suite of arsenide, sulfide, sulfarsenide, and antimonide minerals which include smaltite-chloanthite ($CoAs_2$-$NiAs_2$), domeykite (Cu_3As), safflorite ($CoAs_2$), rammelsbergite ($NiAs_2$), skutterudite ($CoAs_3$), gersdorfite (NiAsS), cobaltite (CoAsS), glaucodot ([Co,Fe]AsS), niccolite (NiAs), dyscrasite (Ag_3S_6), and breithauptite (NiSb), as well as löllingite and arsenopyrite. Uraninite is present in a few of the deposits.

Secondary minerals include the hydrous arsenates annabergite ($Ni_8As_2O_8 \cdot 8H_2O$), erythrite ($Co_3As_2O_8 \cdot 8H_2O$), and scorodite, as well as limonite and manganese oxide. The gangue minerals differ from deposit to deposit and include mainly calcite, dolomite, and quartz and lesser amounts of rhodochrosite, barite, and fluorite.

Native silver and nickel-cobalt arsenide deposits commonly occur in braided vein systems in which the individual veins in general range in thickness from a fraction of an inch to a foot; a very few are as thick as 8 feet. The veins are commonly relatively short, extending only a few hundred feet along strike and dip, but some have been traced for thousands of feet.

Some deposits in shield areas occur along extensive faults or fault-related fractures, but more commonly they are localized by more subtle features, such as fractures that developed parallel to the contacts of sills and other intruded rock bodies and along unconformities underlying locally deposited favorable host rocks. In orogenic belts native silver and nickel-cobalt arsenide deposits have formed at such sites as intersection of fracture veins with flat crushed zones in gneiss or in preferred host rocks such as slate.

Native silver and nickel-cobalt arsenide deposits range widely in size and tenor; individual veins have produced tens of thousands of tons of ore. Arsenic constitutes a significant part of the ore; carload lots of smelter-run material have run as high as 42 percent arsenic, but the average runs about 2–3 percent.

Important producing areas include the Cobalt and Thunder Bay districts of Ontario, Canada (Lang and others, 1970, p. 210–215), the Annaberg and Schneeberg areas of the German Democratic Republic (Lindgren, 1933, p. 602–603), the Andreasberg area in the Harz Mountains of the Federal Republic of Germany (Lindgren, 1933, p. 601–602), and the Kongsberg district, Norway (Vokes, 1960, p. 14–16).

Native silver and nickel-cobalt arsenide deposits originally were considered to be derived from diabase sills, either through differentiation and vein injection, or by diffusion and metasomatic fixation. It was later found, however, that some deposits are located where diabase sills are absent and that where deposits are located near sills, the sills were completely crystallized prior to vein formation. Recently, the restricted lateral and vertical extent of the veins has been interpreted to indicate that the metals were derived from the rocks either cut by the veins or in close proximity to the veins, rather than from a magmatic source. The only rocks sufficiently rich in copper, nickel, and cobalt to supply the metals are greenstone and black pyritic rock interbeded with greenstone. It is theorized that these metals and other relatively rare metals, including arsenic, migrated by diffusion through a static water medium to favorable structural or stratigraphic depositional sites (Lang and others, 1970).

ARSENICAL GOLD DEPOSITS

Arsenical gold deposits occur in the broad shield and lesser areas of Precambrian rock and in orogenic belts.

The lithologic characteristics of the Precambrian terranes differ in detail but are alike in general. Precambrian arsenical gold deposits are mostly in

or associated with felsic volcanic and related intrusive rocks including dacite, andesite, and basalt or their altered equivalents. A few are hosted in metamorphic rocks including quartzite and schist.

The orogenic belts are mostly post-Precambrian sedimentary volcanic and metamorphic rocks which have been structurally deformed and intruded by great masses of granitic rock. Arsenical gold deposits in orogenic belts occur in a variety of sedimentary and volcanic rocks and are associated with felsic and intermediate intrusive rocks.

Arsenical gold deposits commonly contain native gold in quartz and (or) sulfide minerals. Arsenic occurs only in arsenopyrite in most deposits, but in some deposits löllingite also occurs. Arsenopyrite is commonly accompanied by pyrite and (or) pyrrhotite, which together may be as much as ten times as abundant as arsenopyrite. Other sulfide minerals that may be present include chalcopyrite, galena, tetrahedrite, and sphalerite. Scheelite and wolframite occur rarely in some deposits. Sulfarsenide minerals are known but are extremely rare in arsenical gold deposits.

Gangue minerals, except for quartz, which is generally present, differ from deposit to deposit and include ankerite, albite, and tourmaline.

Most deposits occur as replacement veins in or around rock that has been fractured or sheared by faulting. Some deposits are simple in form and occur as single persistent veins that are planar or more commonly curvilinear and of even thickness, whereas others are complex and occur as swarms of lenticular veins, which extend short distances. Deposits which were initially simple in form but which underwent subsequent deformation occur in contorted pipelike or ribbonlike bodies, reflecting the complexity and intensity of deformation. Sulfide minerals in some deposits are evenly disseminated through the vein, whereas in others they are restricted to lenses or pods.

Arsenical gold deposits characteristically are structurally controlled and commonly occur on or along fractured or sheared rock. Some, although obviously emplaced on fault-related structures, are more numerous where the structures transect a particular rock type such as schist, suggesting that the mineralizing process was sensitive to subtle differences in rock chemistry.

The arsenic content of these deposits differs markedly; most deposits within an area or district may contain but a fraction of a percent arsenic, whereas others within the same area or district may contain several percent arsenic. In some deposits the arsenic content is remarkably consistent, and the arsenic occurs in a fixed ratio with gold; in others, the arsenic content diminishes or increases from place to place disproportionately to gold. Arsenical gold deposits may contain as much as 20 percent arsenic, but the average content is no more than 1 percent.

Arsenical gold deposits range from hundreds of tons to several hundred thousands of tons of ore. The Jardine mine, Montana, between 1879 and 1942, produced more than 7 million tons of ore from which 9 million pounds of arsenic was obtained, although this production was for only 8 years of the mine's life. The average grade is estimated to be less than one-half of 1 percent.

ARSENIC SULFIDE AND ARSENIC SULFIDE GOLD DEPOSITS

Arsenic sulfide and arsenic sulfide gold deposits occur almost exclusively in orogenic belts and commonly are associated with Tertiary intrusive igneous or volcanic rocks. Arsenic and mercury sulfide minerals occur together in some deposits. Elsewhere the association is less intimate; deposits of arsenic, mercury, and antimony occur separately but display a regional zonal pattern which suggests a common genesis. Arsenic sulfide minerals are also abundant in some gold deposits.

Host rocks include intermediate and felsic intrusive and volcanic rocks, volcanic sedimentary rocks such as tuffaceous sandstone, and limestone and noncarbonate clastic rocks or their metamorphic equivalents.

Arsenic sulfide deposits are characterized by realgar and orpiment, almost to the total exclusion of other arsenic minerals. Some small vein deposits are composed entirely of one or the other of these minerals. Composite deposits of arsenic sulfide minerals and mercury contain stibnite, cinnabar, metacinnabar, calomel, and native mercury. Arsenic sulfide gold deposits have a more complicated mineralogy; in addition to realgar and orpiment, they contain pyrite, pyrrhotite, marcasite, arsenopyrite, chalcopyrite, scheelite, molybdenite, sphalerite, cinnabar, stibnite, native arsenic, and native gold. The gangue minerals include quartz, fluorite, barite, alunite, sericite, and leverrierite.

Many arsenic sulfide deposits occur as veins that fill fractures and may be tens to hundreds of feet long but which are commonly narrow, generally a few inches to 1 foot thick. Other deposits occur in breccia zones which extend hundreds of feet along strike and dip and are as much as several feet thick. In these deposits, the arsenic sulfide minerals

form a part of the cement around the breccia fragments.

Arsenic sulfide gold deposits occur in vein systems that comprise numerous ore shoots. Such veins measure thousands of feet in length and several hundred feet along the dip, and range in thickness from a few feet to 200 feet. Lenses of realgar and stibnite as much as 20 feet long and 4 feet thick occur in some of the ore shoots.

Both arsenic sulfide and arsenic sulfide gold deposits are controlled by such structural features as fractures, shear zones, or other fault-related structures. The deposits occur as fissure fillings and large-scale replacements. In some deposits or in the deeper parts of some deposits, replacement was nonselective and all strata transected by the veins were affected, whereas elsewhere replacement was selective. Some deposits in volcanic terranes may have been concentrated along the contact of rocks of different permeability.

Arsenic sulfide deposits are small and range from those which have produced a few tens of tons of ore to those which have produced a few thousands of tons. Some of the ore contains as much as 20 percent arsenic but averages only a few percent. Arsenic sulfide gold deposits have yielded tens of thousands and hundreds of thousands of tons of ore; arsenic in these deposits was recovered as a byproduct and constituted a small fraction of the ore, averaging not more than 1 percent.

Examples of arsenic sulfide deposits include several in the State of Washington (Shedd, 1924, p. 51–55). The occurrence of arsenic sulfide minerals with mercury has been reported in Oregon (Brown and Waters, 1951, p. 234) and Alaska (Berg and Cobb, 1967, p. 89–94). Arsenic sulfide gold deposits are best exemplified in Nevada, where several deposits of this type have yielded byproduct arsenic (Hewitt, 1968, p. 872–873; Nolan, 1935, p. 111, 151–156).

Arsenic sulfide deposits are generally considered to have come from sources deep within the crust but to have been emplaced fairly close to the surface at low temperatures. Their occurrence near centers of volcanic activity reflects the common source of mineralizing solutions and flow rocks, both of which are assumed to be differentiates of the same magma (Lindgren, 1933, p. 455).

ARSENICAL TIN DEPOSITS

Arsenical tin deposits occur mostly in orogenic belts, but they occur sparsely in Precambrian terranes. The deposits are closely associated with granitic stocks or batholiths, are commonly emplaced in such bodies or close to their peripheries, and are most numerous near the cupolas or summit areas of the granitic bodies.

Arsenical tin deposits also are emplaced in a variety of sedimentary rocks (sandstone, shale, and limestone), in metamorphic rocks (schist, gneiss, and slate), and in older granitic rocks. No one host rock seems to be more favorable than another.

The ore minerals commonly are cassiterite, native bismuth, bismuthinite, arsenopyrite, and wolframite and lesser amounts of chalcopyrite, pyrite, pyrrhotite, galena, and sphalerite. Hematite, magnetite, and ilmenite occur rarely. The gangue minerals are quartz, which is most abundant, fluorite, lepidolite, topaz, tourmaline, apatite, axinite, and, rarely, beryl or orthoclase. Cassiterite is the principal ore mineral. Arsenopyrite is the only arsenic mineral in this type of deposit.

Arsenical tin deposits occur in veins and pipes. The veins occur in simple planar or undulous form. Some occur in braided systems; others are very irregular and occur in stockworks. They may be as much as 3 miles long, as much as 3,000 feet in vertical extent, and a few inches to several tens of feet thick. They formed by filling of open fissures and replacement of wallrock.

The pipes are roughly circular in plan, range from several tens of feet to more than 100 feet in diameter, and are several hundreds of feet in vertical extent. The ore in some pipes is disseminated, and the walls are indefinite; in others, the contact of ore and wallrock is well defined. In some pipes, arsenopyrite occurs in segregated masses.

Vein deposits of arsenical tin occur in fissures which formed in the chilled shell of congealing granitic plutons and extend into the adjoining country rock. Faulting took place along some of the fissures during mineralization, with the result that composite veins developed.

Some pipe deposits developed along shear zones or other structures, but other deposits do not appear to be located on preexisting structures. It is theorized they were emplaced explosively in the manner of diatremes and were initiated at points of incipient fissuring during a period of extraordinarily high pressure.

The size of arsenical tin deposits ranges from hundreds of tons to hundreds of thousands of tons. The early mined veins, lodes, and pipes were of relatively high tenor, averaging several percent, but because of their depletion, larger but lower tenor deposits are now being worked. The arsenic content of the deposits ranges from a fraction of 1 percent

to as much as 2 percent and is estimated to average not more than 0.2 percent.

Examples of arsenical tin deposits include the Aberfoyle mine, Australia (Connolly, 1953), the Stavoren Fides tin mines, Republic of South Africa (Union of South Africa Department of Mines, Geology Survey, 1959), the Lost River mine, Alaska (Sainsbury, 1964, p. 25), and the mines of the Uncia area, Bolivia (Ahlfeld, 1931, p. 248).

Tin and arsenical tin deposits are generally believed to be products of high-temperature solutions charged with fluorine and boron which acted as strong solvents for metals such as tin and tungsten. The solutions originally constituted a part of the magma, but as the magma cooled, they separated, and subsequently, where fissures developed in the chilled periphery of the magma body, they escaped. The escaping solutions reacted with the fissure walls in the chilled envelope and country rock to form deposits containing fluorine and boron minerals and cassiterite (Ferguson and Bateman, 1912).

OTHER DEPOSITS

Other types of arsenical deposits are known but are not promising as significant sources of arsenic. The types are arsenical quartz, silver, and lead-zinc deposits.

Arsenical quartz deposits are commonly in veins composed of quartz with arsenopyrite and pyrite and, rarely, minor amounts of other sulfide minerals and gold. The arsenical quartz veins represent an early stage of a complex base- and precious-metal mineralization but commonly were emplaced separately from the main-stage ore. They are known in orogenic belts and Precambrian terranes. They are estimated to contain less than 1 percent arsenic.

The arsenical silver deposits described in the literature occur in Precambrian schist in vein systems as much as 1 mile long and more than 1,000 feet wide. The ore includes silver sulfide and sulfosalts, pyrite, arsenopyrite, and very minor amounts of chalcopyrite and gold. The deposits occur in the Randsburg district of Kern and San Bernardino Counties, Calif. (Stewart, 1957, p. 529–530). Deposits of this type may average as much as a few tenths of 1 percent arsenic.

Arsenical lead-zinc deposits are sparse and as a type are best characterized by the Sullivan mine in the Kootenay district of British Columbia (Schofield, 1915, p. 107–108, 131–133; Little and others, 1968, p. 504–505). This deposit formed by replacement of argillitic beds in Precambrian quartzite. The ore minerals are galena, sphalerite, pyrite, pyrrhotite, magnetite, cassiterite, arsenopyrite, jamesonite, and boulangerite. The core of the deposit is composed of pyrite and pyrrhotite. Around the core is a zone relatively rich in lead, silver, tin, and arsenic, and outward from it is a zone rich in zinc and antimony. Deposits of this type, although large producers of base metals, are not sufficiently numerous or rich enough in arsenic to be considered a significant arsenic source; they probably average less than one-half percent arsenic.

RESOURCES

IDENTIFIED AND HYPOTHETICAL RESOURCES

Arsenic resource estimates are based on a limited amount of data. Arsenic has been or is almost entirely obtained as a byproduct of gold, silver-nickel-cobalt, copper, or copper-zinc-lead deposits. The content of arsenic in such deposits is, with few exceptions, only generally known. The arsenic is reclaimed from mill and smelter wastes, and production data are available from only a few deposits. Further, because arsenic is a byproduct, the estimate of arsenic resources is in part dependent on estimates of the resources of the primary commodities and, more importantly, on an understanding of the relation of arsenic to them.

The data base, weak for arsenic resources within the United States, is even weaker for areas outside the United States and is almost nonexistent for countries of the Communist bloc. The resource data are shown in table 9. Resources are considered more

TABLE 9.—*World identified and hypothetical resources of arsenic, in short tons*

	Identified resources [1]	Hypothetical resources [2]
United States	1,300,000	650,000
North America exclusive of United States	500,000	300,000
South America	3,000,000	2,700,000
Eurasia (including insular areas of southeastern Asia)	10,100,000	8,450,000
Africa	2,300,000	1,850,000
Australia	400,000	350,000
World total	17,500,000	14,300,000

[1] Identified resources: Specific, identified mineral deposits that may or may not be evaluated as to extent and grade and whose contained minerals may or may not be profitably recoverable with existing technology and economic conditions.

[2] Hypothetical resources: Undiscovered mineral deposits, whether of recoverable or subeconomic grade, that are geologically predictable as existing in known districts.

than ample to fill the expected demands until the year 2000.

The assumptions that serve as a basis of treatment are as follows: of the gold resources, 5 percent are considered to be arsenical and to have an average ratio of arsenic to gold of 2,000:1; of the resources of copper and copper-zinc-lead, 15 percent are considered to be arsenical with a ratio of arsenic to

copper of 1:50; of the resources of cobalt, 3 percent are considered to be arsenical with an average ratio of arsenic to cobalt of 2:1; and of the tin resources, 10 percent are considered to be arsenical with an average ratio of arsenic to tin of 10:1.

Several factors stemming from the relation of arsenic to primary metals are considered when calculating the various arsenic-metal ratios. For example, arsenic does not occur in placer deposits of gold or tin or in gold deposits hosted by Precambrian conglomeratic sandstone. Gold placer deposits can be disregarded for they are a relatively small source of gold and the absence of arsenic from them is of little account in the estimate, whereas tin placer deposits are an important source of tin and the absence of arsenic from them seriously affects the estimate. Gold deposits in ancient conglomeratic sandstone deposits are the most important source of gold, and the absence of arsenic from them drastically affects the estimate. The ratio of arsenic to cobalt was weighted to favor arsenic in order to account for the additional arsenic that is combined with nickel, copper, and iron in native silver and nickel-cobalt arsenide deposits. Lateritic deposits of nickel and cobalt are disregarded as sources of arsenic. Such deposits may have in part been derived from primary deposits of native silver and nickel-cobalt arsenides, but arsenic apparently escaped in the weathering process.

The resource figures for arsenic shown herein were largely derived from data for gold, copper, and other base metals published in other chapters of this volume. Each of the continental areas is assumed to contain sufficient resources of some of the more important types of arsenic-bearing deposits so that general estimates accurate within an order of magnitude can be made. The hypothetical resources of arsenic are estimated to be equal to the total of identified resources of arsenic occurring with base metals plus one-third the identified resources of arsenic occurring with the gold.

Arsenic is currently produced in about 25 countries. The types of arsenic-bearing deposits and the countries in which they occur are shown in table 10.

TABLE 10.—*Types of arsenic deposits of the world*

Type of deposit	*Areas*
Enargite-bearing copper-zinc-lead deposits.	United States, Argentina, Chile, Peru, Mexico, Republic of the Philippines, Spain, Yugoslavia, U.S.S.R.
Arsenical pyritic copper deposits.	United States, Sweden, Federal Republic of Germany, Japan, France, U.S.S.R.
Native silver and nickel-cobalt arsenide-bearing deposits.	Canada, Norway, German Democratic Republic, Czechoslovakia.
Arsenical gold deposits	United States, Brazil, Canada, Republic of South Africa, Australia, U.S.S.R.
Arsenic sulfide and arsenic sulfide gold deposits.	United States, People's Republic of China.
Arsenical tin deposits	United States, Bolivia, Australia, Indonesia, Malaysia, Republic of South Africa.

SPECULATIVE RESOURCES

Arsenic deposits which may form by the mobilization, concentration, and redeposition of arsenic in favorable geologic environments could be an additional resource of arsenic.

Most of the arsenic or arsenical deposits that have been discussed here are types which were derived from magmatic or magma-related sources; a few, however, were derived from adjoining host rocks. Studies of ancient rock terranes show that certain types of ore deposits are broadly related to certain rocks, and studies of sulfur isotopes indicate that metals in disseminated sulfide minerals in the surrounding rocks were the likely source of metals concentrated in the ore deposits. The metals were mobilized when sufficiently energized and then moved by diffusion through the rock and accumulated in favorable structures.

Under local favorable conditions in areas where the rock has a high arsenic content, arsenic or arsenical deposits might be found. Geochemical studies show that shale averages 5–15 ppm arsenic and that sulfide-rich organic shale of marine origin contains even greater amounts. Although organic-rich shale is widespread and has formed in many geologic periods, the number of ore deposits found in it is few. The few that have been found may have formed under exceptional circumstances in which metals became highly concentrated in sea water. Rather than investigate organic-rich shale units on a broad basis, efforts should be concentrated on areas that have been subjected either to extreme structural deformation and (or) to metamorphism or that have been intruded by large bodies of igneous rock. In such areas, the metals may have been mobilized and concentrated in favorable structural settings. These areas are likely to be regional in scope and to be recognizable from stratigraphic, structural, and other geologic relationships. Such areas include parts of depressed belts or geosynclines, which are the locales of organic-rich marine shale. Other such areas include ancient crystalline terranes where graphitic schist, the metamorphic equivalent of organic-rich shale, is present.

The amount of arsenic in organic shale is estimated to total about 10^{11} tons; if as much as 0.01 percent of this arsenic is concentrated in minable

deposits, about 10 million tons should be a recoverable resource.

PROSPECTING TECHNIQUES

Arsenic has not been and is not a sought-after commodity; it is produced as a byproduct of other commodities—gold, silver, or copper—and consequently, no prospecting endeavor has been aimed solely at finding it, although techniques suitable for finding other commodities are well suited for finding it.

Some small arsenic deposits containing realgar or arsenopyrite were no doubt found by recognition of the ore minerals or their gossans in place, in float, or in stream gravels. The Boliden arsenical copper deposit in Sweden was found by an electrical geophysical method following the discovery of sulfide boulders in till which blanketed the region. Arsenic in soils and stream sediments may be detected by geochemical methods and has been used as a guide to other metals, including cobalt, tungsten, gold, and silver; as such, it can be used as a guide to arsenical metal deposits. Its mobility, however, is restricted by the presence of high iron in soils and stream sediments.

PROBLEMS FOR RESEARCH

Because arsenic historically has been sufficently abundant to meet human needs and has been obtained almost wholly as a byproduct of other commodities, it has not been intensively studied. The ever-persistent problem of supply of most other commodities will eventually include arsenic. Research is needed so that the geologic relations of arsenic can be better understood and guides can be found for the discovery of new deposits.

Much fundamental background knowledge on arsenical deposits is needed. Arsenic minerals which occur in many ore deposits are reported only in a cursory manner, and only rarely are estimates of their proportions to the associated metals given. Also the relationship of arsenic to primary or host commodities needs additional study. Arsenic occurs randomly with several metals including gold, copper, and tin, but its occurrence with these metals is not fully understood. Further study might make possible more accurate predictions of the occurrence of arsenic with these metals on a districtwide or regionwide scale.

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ASBESTOS

By Andrew F. Shride

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ABSTRACT OF CONCLUSIONS

The fibrous silicate minerals grouped in commerce under the term "asbestos" are essential to modern technology in certain relatively low-volume uses. Asbestos-cement products consume 70 percent of world output, and expanded demand in this field is anticipated. Universally, asbestos-cement building materials are especially suited for new construction of housing and industrial plants; in industrial nations the asbestos-cement pipe for use in sewage and water systems is in particular demand. The United States is the principal fabricator and consumer of asbestos products and currently imports 85 percent of the raw asbestos needed to sustain its large industry.

Chrysotile asbestos constitutes 93 percent of world asbestos trade, and Canada has been the principal supplier of world needs since asbestos was first used on a large scale. Canada continues to have the largest reserves of chrysotile, and its fields hold the greatest promise of any in the Americas for finding additional resources. Since World War II, the U.S.S.R. has increased its chrysotile-asbestos-producing facilities and has found resources to approach those of Canada. Ninety percent of world resources of chrysotile are in Canada, Russia, and the nations of southern Africa.

Crocidolite and amosite make up about 3½ and 2½ percent, respectively, of world asbestos commerce; anthophyllite, tremolite, and actinolite apparently make up only a fraction of 1 percent. Most of the world reserves, and the only sources currently exploited, of crocidolite (blue) asbestos are in the Transvaal and Cape Provinces of the Republic of South Africa. The only source of amosite is in the Transvaal. Domestic resources of anthophyllite and tremolite, little used in the United States, are apparently adequate for U.S. needs.

INTRODUCTION

The geologic potentials for asbestos resources most likely to be available for consumption in the United States during the next several decades are the prime concern of this report. Technologic aspects necessary to a general understanding of the asbestos industry are not discussed here except as required to define terminology peculiar to the commodity. For those who wish to delve further, review articles that cover all facets of the industry are cited; where available, recent reports that update the reviews are also noted. A selected bibliography of asbestos literature extant as of 1955 is available (Avery and others, 1958), as is a map showing the location of asbestos occurrences in the conterminous United States (Chidester and Shride, 1962). For general background two review articles by

Jenkins (1949, 1960), which are complementary in their coverage, are recommended. Condensed comparisons of worldwide scope of subjects such as mining and milling methods, grading and classification, and production and consumption trends have been furnished by Bowles (1959). Updated discussions of trade and use trends are available in two articles in Industrial Minerals (1970a, b).

DEFINITION AND PROPERTIES

"Asbestos" is a term applied in commerce to naturally fibrous silicates that are amenable to mechanical separation into fine filaments of considerable tensile strength and flexibility; these fibers have, by virtue of unique combinations of physical and chemical properties, a great variety of industrial uses. Manmade fibers and naturally occurring organic fibers do not possess the full range of properties inherent in asbestos, and thus—at best—can be substituted only partially for the mineral fibers (Carroll-Porczynski, 1958). Chrysotile, the fibrous form of serpentine, constitutes about 93 percent of world asbestos production. The other five asbestiform minerals ordinarily used are amphiboles. In order of quantities consumed, they are: crocidolite and amosite, which respectively make up about 3½ and 2½ percent of asbestos commerce; anthophyllite and tremolite which probably make up only a fraction of 1 percent of the asbestos used; in recent decades, actinolite, the least used, has seldom been given note in the trade. These use ratios mainly reflect desirable physical properties; crocidolite and amosite do have particular properties that would favor greater use if they occurred more universally and in larger amounts.

The properties primarily of concern in evaluating asbestos as to ultimate use are: (1) flexibility, (2) length of fiber, (3) tensile strength, (4) chemical reactivity, (5) resistance to heat, (6) electrical conductance, and (7) filtration characteristics. (See Badollet, 1951 and 1953, for comparative properties of asbestos species.) The use of a given lot of asbestos is governed by acceptable properties which are determined largely by fiber length. The longest fibers demand the highest prices and the shorter grades progresively are lower in value. (In recent years soft chrysotile fibers ¾-inch long have sold for $1,500–$1,600 per ton, whereas the shortest grades have brought $50–$100 per ton.) Thus, asbestos should be separated from the parent rock, fiberized, and classified by length with attention given to a minimum of breakage.

By virtue of variations in physical properties, a given mineral is put to very different uses. Soft, silky chrysolite of adequate length fabricates into textiles. The same fiber, because it forms a slurry that can be dewatered only slowly, is unsuitable for processing as the binder in cement products. Harshness—that is, resilience like a broomstraw when flexed—makes chrysotile very unsuitable for textile use but greatly enhances the manufacture of chrysotile into asbestos-cement products. Some desirable combinations of properties are limited in occurrence. An example of strategic concern is textile-quality chrysotile of low iron content for heat-resistant electrical insulation. Physical characters ordinarily overlooked can be significant. Resources recently developed near Coalinga, Calif., are illustrative. For decades large parts of an extensive serpentine mass in this area had been recognized in the form of minutely sheared incoherent leathery flakes, quite lacking resemblance to typical asbestos ores. On appraisal in the late 1950's, the flaky material proved to contain high proportions of microscopic fibers, all of the shortest lengths ordinarily recovered in the processing of ordinary ores. Further, these fibers had special attributes of being superior in whiteness—thus being particularly suited as binders for floor tiles—and of capacity to absorb hydrocarbons.

USES

Asbestos is widely stated to be a constituent in at least 3,000 manufactured products. It is a particularly critical material in friction materials and in electrical insulation, where resistance to moisture, flexure fatigue, and abrasion and a capacity to absorb resins can be as important as heat and flame resistance. Asbestos is important as an abrasion- and corrosion-resistant binder or reinforcing material in products made of rubber or plastic and mixed with lubricants or other compounds used in packings or gaskets, where an inert material is required owing to exposure to superheated steam, acids, alkalis, oil, or seawater. Laminated as paper or in textiles, it is fabricated into products that are immune to attack by fungus, bacteria, or vermin and that are not affected by alternate wetting and drying. Asbestos fibers can be finely divided; and, separated in optimum degrees, they are superior inert mediums for filtering gases and liquids. This partial listing only superficially indicates the many asbestos-bearing products essential to our modern way of life; actually such products account for less than one-third of asbestos consumption.

About 70 percent of U.S. and world consumption of asbestos is in asbestos-cement products. Indeed, the demand for shingles, roofing, wallboard, flat and

corrugated sheets, and pipe is increasing more rapidly than that for other asbestos products. Since World War II, new asbestos-cement plants have been built throughout the world. Most of the lesser industrialized nations, as well as many of the emerging nations, now have manufacturing facilities. The lack of a domestic or nearby source of asbestos is no great deterent to this trend, because processed asbestos makes up only 15–20 perecnt of the locally finished product, which is competitive in cost for low-cost housing and is universally suitable as building material. In the United States, the demand for asbestos-cement pressure pipe, mainly for use in sewage and water systems, has increased even more rapidly than the need for other asbestos-cement products. The demand in Europe, where such pipe was used extensively long before it came into common use in the United States, is also increasing. Thus, the demand for the medium- to short-length chrysotile fibers (groups 4, 5, and 6—see Bowles, 1959, or Jenkins, 1960, for summary of classifications commonly in use) and equivalent crocidolite and amosite fibers is bound to escalate wherever population or industrial expansion occurs. Demand in the United States is likely to keep pace, as long as per capita consumption of water increases and pollution control forces the construction of more sophisticated sewage disposal systems.

Actually, perhaps at least half of the remaining 30 percent of asbestos consumed is also keyed to the construction industry. In the United States, floor tiles account for 10 percent of consumption; paints, electrical insulation, steam-pipe coverings, and other low-volume uses probably account for several percent.

EXPLOITATION

Asbestos was first produced in Quebec in 1878, and within a few years this source dominated world production. The firm establishment of an asbestos fabricating industry and markets in America by 1900 awakened interest in asbestos mining throughout the world. By 1910, notable asbestos-mining facilities had been established in the countries that since have become the centers of world production. Although asbestos occurrences are widely dispersed throughout the world, and mining is recorded at several widely separate localities on every continent except the polar landmasses, most of world production has been from three areas. In order of productivity these are: (1) Canada, (2) the U.S.S.R., and (3) the southern Africa fields centered mainly in Rhodesia and the Transvaal and the Cape Provinces of the Republic of South Africa, but with significant increments from one district in Swaziland. Before 1950, 90–95 percent of the reported world annual production was from these three areas. In 1968, they furnished about 84 percent; the United States, Italy, and mainland China probably produced another 10 percent, and 17 other nations accounted for most of the remainder.

The dominance of Canada in the asbestos trade is apparent in several ways. The largest asbestos mines and mills in the world are in Quebec; as a consequence, specification standards that affect commerce are in great part determined there. Before the mid-1950's, more than half of world production was in Canada; and for several years, output from Canada exceeded 60 percent and even approached 70 percent of world supply. Despite a 65-percent jump in productivity since 1950, Canadian shipments have been increasing at a lower rate than total world production; consequently, Canada has accounted for about 45 percent of the annual total in recent years. Canada consumes less than 5 percent of its output, and in supplying raw asbestos to more than 80 countries it accounts for 70–75 percent of world exports. Russia, the second largest producer and the only nation that is both a large producer and a large consumer, during recent years has exported about 15 percent of its production, mainly to eastern European nations. Until recently Rhodesia was the second largest exporter of asbestos to the Western World.

The United States has long been the principal fabricator and consumer of asbestos products, but has always been dependent on imports of raw asbsetos to sustain its large industry. During many years prior to 1955, the United States consumed 45–55 percent of world output and domestic sources supplied only 3–8 percent of annual requirements. With the larger scale production of short chrysotile from California that started in 1962, domestic production more than doubled and current annual output of 125,000–130,000 tons represents about 15 percent of United States consumption. Before this increase, in terms of tonnage, 90–96 percent of United States imports was chrysotile asbestos from Canada, and these imports represented 70–75 percent of Canadian production. Thus, for a considerable time, as shown in figure 9, United States consumption was reflected in the Canadian production record. Before 1950, Rhodesia furnished most of certain textile grades of chrysotile.

The United States is wholly dependent—as are all nations—on the Transvaal for amosite asbestos and on the Transvaal and Cape Provinces of South Africa for all but a small part of crocidolite (blue)

asbestos needs. The American asbestos-cement industry has become particularly reliant on crocidolite because a small content of these fibers blended with chrysotile facilitates manufacture. For several decades there was speculation that large resources of crocidolite existed in the remote Hammersley Range of Western Australia. The first significant mining of these deposits began in 1947; concurrently intensive exploration was done through large parts of an area about 200 miles long by 75 miles wide. Ore seams were found to be thin and not generally extensive, and continuity was difficult to predict. Crocidolite mining was recessed in 1966, apparently because the readily won resources had been largely depleted. Some 400,000 tons of crocidolite are outlined to be recovered when access and other circumstances are more favorable. Submarginal resources of crocidolite have been estimated at 2 million tons (Trendall and Blockley, 1970). Thus, some doubt exists that the Australian crocidolite resources can significantly supplement those of the Republic of South Africa.

Since 1940, the increase in worldwide demand for asbestos has been exceptional; more remarkable has been the ability of the industry to discover and rapidly develop resources to keep pace. These events are in part depicted on figure 9. Between 1940 and 1950, U.S. consumption doubled, paralleling the world trend, then leveled to average about 750,000 tons annually. With the impetus provided by the postwar escalation of production capacity and in view of the potential created by universal acceptance of asbestos-cement products, Canadian producers successfully searched out new markets and continued to increase production, thus breaking the long-established pattern of production parallel with U.S. consumption.

While Canada increased production by more than 400 percent, from 375,000 tons in 1940 to 1,650,000 tons in 1970, similar expansion occurred in the other major producing areas. Data for the U.S.S.R. are scant; therefore, the production record shown on figure 9 is incomplete. Nonetheless, the order of the increase in U.S.S.R. production, from 100,000 tons in 1940 to 1,150,000 tons in 1970 is of the correct magnitude. With due allowance for exports, consumption of asbestos in the U.S.S.R. may have reached a par with U.S. consumption during the late 1960's. Rhodesian production of chrysotile asbestos, about 58,000 tons in 1940, apparently tripled by the late 1960's. In the Republic of South Africa, where chrysotile makes up about 15 percent, amosite about a third, and crocidolite something over half the output, production increased from 27,400 tons in 1940

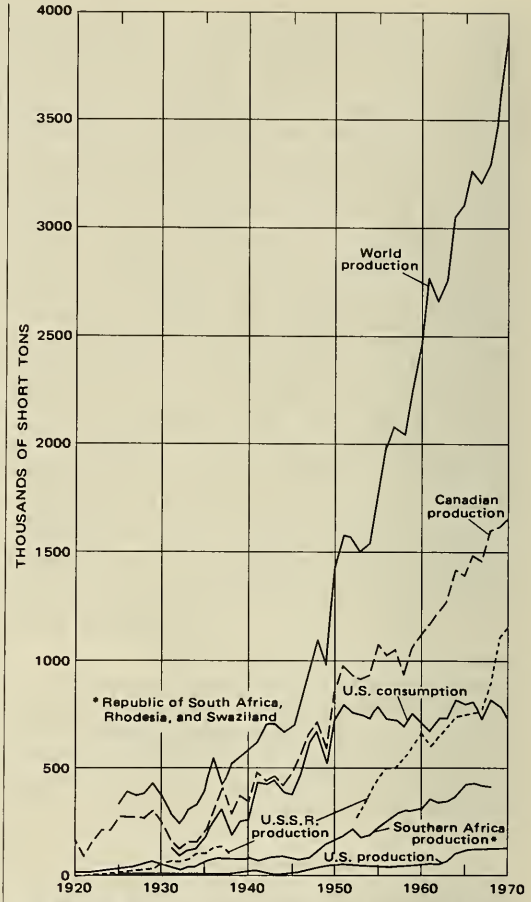

FIGURE 9.—World production, production from major sources, U.S. production and consumption of asbestos, 1920–70.

to about 280,000 tons in 1970. South African output surpassed Rhodesia production for the first time in about 1950. Several nations that mined only small amounts of asbestos or mined only sporadically also have expanded production to significant tonnages in recent years.

GEOLOGY

MODES OF VEIN OCCURRENCE

Asbestos occurs as cross-fiber veins, in which the parallel fibers are about normal to the vein walls; as slip-fiber, in which fibers lie in near-parallel arrangement, commonly somewhat matted together, along the plane of the vein—commonly also an obvi-

ous plane of slippage; or as mass-fiber, which is an aggregation of variously oriented fibers or stellate groups of radially arranged fibers. Most cross-fiber veins are split by one or more partings about parallel to vein walls; as a result, most of the fibers of this mode of occurrence are considerably shorter than vein width. Asbestos of the cross-fiber mode is the type most readily separated from enclosing rock and prepared for use. Slip-fibers may be of considerable length and flexibility, but commonly present difficulties in preparation. Chrysotile, crocidolite, and amosite occur mainly as the cross-fiber type. Some slip-fiber is found in most chrysotile deposits, and from a few it is the principal type recovered. The remaining asbestiform amphiboles—anthophyllite, tremolite, and actinolite—occur mainly as mass-fiber or slip-fiber, are least amenable to separation, and commonly are brittle or weak and therefore limited in use. The rare deposits that do include these minerals as strong flexible fibers in cross-fiber veins contain them in very small amounts.

GENERAL SETTINGS

Chrysotile asbestos the world over occurs in two geologic settings of different type. Chrysotile is won mainly from large stockworks of veins in serpentinized peridotite, pyroxenite, and dunite, collectively termed "serpentinites." From some of their prime occurrences these deposits can be termed the "Quebec type." Chrysotile asbestos is mined secondarily from deposits of the Arizona type, in which the veins are confined to thin serpentine layers in limestone.

Anthophyllite and tremolite asbestos deposits occur in ultramafic intrusions and in associated greenstones and amphibolites; thus, their gross geologic setting parallels that of the principal chrysotile deposits. The deposits are small and erratic in distribution and in character of fibers.

Crocidolite and amosite occur only in certain fine-grained cherty ferruginous metasediments of the sort commonly designated "banded ironstones" or "banded iron formation." The banded iron formations that host crocidolite occurrences are additionally distinctive in that aggregates of sodium-rich minerals occur in certain layers. Such geologic settings are known in only a few localities worldwide, and in still fewer places have geologic processes coincided in such a way as to bring about the formation of crocidolite and amosite (Cilliers and Genis, 1964). Locally in the northern Transvaal, amosite and crocidolite occur together (Cilliers, 1964). The only exploited deposit of crocidolite in the Western Hemisphere, and the only recognized potential source other than the South African and Australian occurrences previously mentioned, is in a remote part of east-central Bolivia. Reportedly, blue asbestos from Bolivia lacks tensile strength inherent in the crocidolite from other sources.

CHRYSOTILE DEPOSITS IN MASSIVE SERPENTINITE

REGIONAL SETTINGS OF PRINCIPAL NORTH AMERICAN DEPOSITS

The zone of ultramafic rocks in the Appalachian belt of eastern North America is a prime example of the regional setting found wherever chrysotile deposits of the Quebec type exist. Hundreds of ultramafic intrusive masses, ranging from essentially concordant lenses and sills a few tens of feet wide and of no great length to thick irregular tabular or bulbous masses with maximum dimensions measurable in miles, are confined to a belt that is commonly less than 5 miles wide, that is only in a few places more than 25 miles wide, and that stretches northeast from Alabama to Newfoundland along a sinuous trace of more than 2,000 miles. This trace marks the site of an ancient fold mountain belt, which began as a eugeosynclinal trough that—starting in Late Ordovician time—accumulated a thick sequence of sediments, which were indurated, were invaded by intrusive masses, and were complexly folded. The belt was terminated as mountain terrane in Middle Devonian time.

The ultramafic rocks of this and other asbestos-bearing belts are dominated by peridotite, but include much dunite and pyroxenite. These ultramafic rocks are commonly much altered to form serpentinites, and are intricately juxtaposed with basaltic volcanics, diabase, and gabbro to make up complexes that have been termed "ophiolites." The ophiolites of orogenic (mountain-forming) belts are generally designated as the "alpine type" (Thayer, 1967). The genesis of the alpine-type ophiolites, and especially the mode of transport and emplacement of the serpentinites, long has been the subject of spirited debate; the debate has been accelerated particularly during the last decade with the rapid evolution of concepts of global tectonics. Early workers regarded peridotite, pyroxenite, and dunite as rock types directly crystallized from a magma; the lack of associated thermal metamorphism and other magmatic features ultimately forced the conclusion that alpine-type serpentinites were emplaced in their present host rocks at low temperatures and probably in the solid state (for review, see Chidester, 1962). Recent hypotheses—in various versions—propose that serpentinites represent slabs of ultramfic mantle ripped

from the base of the thin ocean crust and transported tectonically to be emplaced along margins of the continents. Coleman (1971) reviews such concepts; Bailey, Blake, and Jones (1970) discus pertinent ophiolites in California. Certain large alpine-type serpentinite masses are almost certainly sedimentary accumulations derived from tectonically transported mantle material (Lockwood, 1971).

The restriction of asbestos-bearing terranes to short increments of the Appalachian belt is typical of most ophiolite belts. Veinlets of chrysotile may be seen sporadically in many ultramafic masses of the Appalachians. Until recently, the only minable concentrations were found along a 55-mile segment that trends northeast in the Eastern Townships of southeastern Quebec. (See Cooke, 1937; Riordon, 1957.) Farther northeast, noteworthy prospects have been found; but only one major deposit, near Baie Verte on the north coast of Newfoundland, has been opened—and that only in the last decade. To the south, the Belvidere Mountain deposits of northern Vermont are the only minable deposits to lie outside the Eastern Townships, Quebec, interval. South in the Appalachian belt beyond Staten Island, N.Y., no chrysotile occurrances that would warrant more than cursory exploration seem to be present.

A wholly separate ophiolite terrane of Precambrian age is exposed widely in eastern Ontario and extends eastward into western Quebec. Large-scale chrysotile asbestos production in Ontario began with opening of the Munro mine in 1950. Since then, widely separate serpentinite masses in this older terrane have been targets of much exploration and of mine development which is still current.

A longer, much broader, and structurally more complex belt of ultramafic bodies, emplaced during Mesozoic time, crudely parallels the Pacific Coast of North America. The best known interval is in California where numerous small to very large serpentinite masses occur (1) in the Coast Ranges from southern part of the State to southwestern Oregon, (2) to the east of the Coast Ranges across the Great Valley of central California in the western foothills of the Sierra Nevada, and (3) and in especially wide exposures in the Klamath Mountains of northwestern California (Bailey and others, 1964). Serpentinites of a presumed offset extension of the belt occur in east-central Oregon. Next seen in scanty occurrences east of Puget Sound along the Cascades of northern Washington, the belt continues north-northwest through central British Columbia and Yukon Territory to the vicinity of Dawson. Sub parallel to the British Columbia portion and 80–160 miles west, along the panhandle of southeastern Alaska, is a separate noteworthy belt, 30 miles wide and almost 400 miles long, of zoned ultramafic bodies (Taylor and Noble, 1960). These bodies are little serpentinized and apparently lack chrysotile deposits. The continuation of the main belt in an arcuate trend northwest and perhaps west an undetermined distance into central Alaska is poorly known. As yet, only a few large deposits of asbestos have been recognized in the Pacific belt.

LOCALIZING FACTORS

The succession of geologic events (Cooke, 1937; Riordon, 1957) that culminated in the formation of chrysotile deposits in southeastern Quebec is typical of events wherever large deposits occur. Two stages of serpentinization are recognized. The first stage was pervasive but incomplete and apparently occurred during initial cooling of magma or while solid ultramfic masses were being emplaced. Peridotite, which is the principal host for asbestos veins, and pyroxenite were only partly altered to serpentine; commonly, dunite segregations were converted rather thoroughly to serpentine. Much later, after or near the end of an episode of deformation that modified the structural disposition of the intrusive bodies, all ultramafic rocks in the vicinity of shear zones and associated faults and fractures were altered almost completely to serpentine. The stockworks of chrysotile veins that make up the deposits were formed during this second episode. A final episode of hydrothermal activity resulted in the formation of talc schist, steatite, and massive quartz-carbonate bodies. These materials are largely confined to major shear zones that transect the serpentinites and to sheared margins of the masses. In places, the asbestos was deleteriously altered by the talc-forming process.

Most of the Quebec deposits border or contain small acidic intrusions which range from granite to albite syenite in composition. The parts of the ultramafic masses that border the granitic masses may be intricately fractured and thoroughly serpentinized. A few instances of chrysotile veining granite have been noted. These relations cause many investigators to believe that acid intrusions had a part in the genesis of chrysotile concentrations. This hypothesis is not universally upheld, however, probably because many chrysotile deposits exist that do not show obvious association to granite.

The location, form, and size of individual chrysotile deposits in great part have been determined by the configuration of major faults and by the volume of peridotite affected by subsidiary faults and fractures; both of which in turn reflect the relative com-

petencies of contiguous rock units. Riordon and others (1957) provide descriptions that permit comparisons of individual deposits. Major persistent shear zones in serpentinite are largely barren of asbestos; but stockworks of asbestos veins occupy intricately fractured rocks that border these shear zones. Similarly, thoroughly serpentinized aureoles adjacent to acid intrusions and completely altered dunite bodies tend to fail by shearing and flow; in response to the resultant stresses the more competent peridotites adjacent to these masses developed and sustaind complex networks of open fractures in which chrysotile was formed. Where peridotite masses have considerable breadth, the chrysotile deposits commonly hug a margin of the peridotite mass, reflecting again the tendency for optimum fracturing to occur where contrasts in rock competency exist. Several of the larger deposits occur where an irregularity in the plane between peridotite and host rock influenced the trend and distribution of faults. Others occur in "wedges" of fractured peridotite where throughgoing shear zones converge along strike or dip.

SIZE, SHAPE, AND ASBESTOS CONTENT

Ore bodies are irregular in outline, may be erratic in asbestos content so that margins of ore bodies are sharp to ill defined, and range considerably in size. In Quebec, the minimum dimension of rudely ellipsoidal bodies is about 400 feet. Lenticular bodies are 200–2,500 feet thick and have maximum dimensions of 1,000–5,000 feet. Most of these bodies bottom at depths of 400–1,000 feet, but one major ore shoot extends to a depth of at least 1,800 feet. Individual deposits currently mined in Quebec originally contained 10–200 million tons of ore. A very exceptional deposit, the site of the Jeffrey mine with production capacity since the mid-1950's in excess of 500,000 tons of fiber per year, still has ore reserves on the order of 500 million tons.

Asbestos content and quality vary. Most ore bodies are stockworks of cross-fiber veins; in some tabular bodies, veins, disposed in parallel, ribbon large parts of the serpentinized peridotite. Some cross-fiber veins are 6 inches or more thick, but all except a small proportion are less than ½ inch wide; ribbon-vein occurrences in particular may average much less. Thus, one deposit may consistently yield short fibers; whereas another yields various lengths. Similarly, some deposits are rather uniform in quality of fiber; others contain both harsh and soft fibers.

Deposits with an overall asbestos content of 1½–2 percent have been mined; some deposits locally have contents as high as 25 percent; the typical occurrence has an overall content of 5–7 percent. Thus the deposits are of sizes and proportions amenable to large-scale open-pit or underground mining methods, and in some instances only large-scale operations would permit the economic recovery of a range of variable ores.

CHRYSOTILE DEPOSITS IN LIMESTONE

The Arizona type of chrysotile deposit is made up of one or more tabular asbestos-bearing zones 6–8 inches thick and of small areal extent. These tabular lenses were localized where cherty or otherwise siliceous magnesian limestones were metamorphosed adjacent to igneous intrusions—in most instances sill-form intrusions of gabbro or diabase. The Arizona-type deposits are mostly of small tonnage and are amenable to mining only by small-scale, high-cost methods; but the asbestos content of the ore is high, long fiber predominates, and low iron content is characteristic. Thus asbestos from the Arizona-type deposits can complement the short magnetite-rich chrysotile characteristic of most Quebec-type deposits.

ASBESTOS RESOURCES IN NORTH AMERICA

A review of exploration activities provides a basis for an optimistic view that many geologically favorable sites remain to be prospected and that known occurrences have not everywhere been widely or deeply enough explored. No attempt is made here to appraise asbestos resources outside North America. The following summation of the resources in the United States and contiguous areas (table 11) is probably conservative.

TABLE 11.—*Chrysotile asbestos resources of North America, in short tons of fiber*

	Identified resources [1]	Hypothetical resources [2]
Canada	70,000,000	35,000,000
United States	[3] 3,700,000	2,000,000
Mexico	1,500,000	

[1] Identified resources: Specific, identified mineral deposits that may or may not be evaluated as to extent and grade, and whose contained minerals may or may not be profitably recoverable with existing technology and economic conditions.

[2] Hypothetical resources: Undiscovered mineral deposits, whether of recoverable or subeconomic grade, that are geologically predictable as existing in known districts.

[3] Exclusive of Group 7 resources in California, see under "United States."

CANADA

Canadian production prior to 1950 was almost exclusively from the Eastern Townships of Quebec. Since 1950 the volume of reserves outlined in Ontario, British Columbia, Yukon Territory, Newfoundland, and other parts of Quebec has increased steadily, and about 15 percent of Canadian production is from these sources. Considerable additions also have been made to the known reserves in the

Eastern Townships, and this established district contains at least three-quarters of identified Canadian reserves. Much of the terrane encompassing the more recently exploited deposits is yet to be evaluated geologically. Pending determination that the later developed asbestos-bearing areas are as consistently geologically favorable as the Eastern Townships belt, the latter must continue to be regarded as the most promising area in the Americas for undiscovered resources.

The first deposit opened in northern Ontario was depleted within 15 years, but other deposits in the general vicinity are taking its place, and continuing exploration provides promise for additional exploitable resources in that area. The Precambrian terrane that is host to these occurrences is structurally complex and commonly poorly exposed, and the potential asbestos deposits require rigorous geologic study and extensive drilling programs for evaluation. None of the Ontario occurrences have yet been shown to have the potential of the larger deposits of the Eastern Townships belt.

Occurrences elsewhere in eastern Canada do show promise of sustaining large-scale operations. Significant reserves have been outlined in Maizerets Township and near Chibougamau, respectively about 300 miles northwest and north of Ottawa, and in a third deposit 800 miles farther north on the Ungava Peninsula. If viable mining operations materialize in these three widely separated localities in Quebec, they may well give the impetus to search out additional large resources in the Precambrian ultramfic terrane of the province.

Soon after mining of the Advocate deposit, on the north coast of Newfoundland, began in 1963, a yield in excess of 60,000 tons of fiber annually was established. With expansion of facilities, production of 100,000 tons annually is anticipated. The success of the Advocate development may spark continued prospecting of the many ultramfic bodies of Newfoundland.

The discovery in 1950 of the Cassiar deposit on McDame Mountain in northern British Columbia, and subsequent rapid implementation of the mining operation—which started in 1953 despite problems such as rigorous climate, permafrost, and transportation logistics related to remote location—stimulated search for other deposits in the northern part of the Pacific Coast ultramafic belt. The Cassiar reserve, of some 25 million tons of ore with a content of 8–10 percent asbestos that mills free of magnetite and includes a high proportion of long fibers, has eliminated long-standing dependence on Rhodesia for strategic low-iron textile fibers. Comparable reserves were ultimately outlined at the Clinton Creek deposit, 65 miles northwest of Dawson City in the Yukon Territory and within 9 miles of the Alaskan border, and mining started in 1968. The Cassiar and Clinton Creek mines furnished more than 10 percent of Canadian production in 1969–70. West-northwest of the Clinton Creek deposit and as much as 80 miles into Alaska a few occurrences of chrysotile have been reported (Foster, 1969). That part of the ultramafic belt that extends through interior British Columbia, across Yukon Territory and perhaps 150 miles or more into the Yukon-Tanana upland of east-central Alaska is a prime target for much geophysical and geologic evaluation.

UNITED STATES

Prior to the early 1960's, about 80 percent of the asbestos produced in the United States had been mined from deposits on Belvidere Mountain, near Lowell in northern Vermont. Currently about 40,000 tons of medium- to short-length chrysotile fibers are produced annually from those deposits. Reported reserves are more than 1 million tons of fiber. This remains the only locality in the Appalachian belt within the United States where minable concentrations of chrysotile asbestos are known or are likely to be found. Along the southern part of of the belt, particularly in western North Carolina (Conrad and others, 1963) and northeastern Georgia (Bowles, 1955, p. 25–26), many small deposits contain in aggregate an anthophyllite resource of more than 100,000 tons.

Although the ultramafic rocks of California have been much prospected and intermittently yielded small quantities of asbestos after 1882, no mining operation of large scale was developed until 1962, when a plant with a capacity of 2,500 tons of ore per day began operation on a deposit near Copperopolis in Calaveras County. The unusual short-fiber deposits in eastern San Benito County and western Fresno County, northwest of Coalinga, also were first exploited in 1963. California immediately became the principal asbestos-producing State and currently furnishes more than 75,000 tons of chrysotile fibers annually.

The host for the occurrences near Coalinga is an intensely sheared mass of serpentinite 14 miles long and 4 miles wide. The chrysotile occurs as fibers largely indiscernible to the eye that are matted in leathery flakes along closely spaced shear planes. Chrysotile occurs extensively in this form in the southeastern half of the serpentinite mass. Fiber content is highly variable, but locally exceeds 50

percent; large ill-defined masses of the leathery material that will yield 20–25 percent fiber in the milling process is considered ore. Only fiber of Group 7 grade is recovered. Obviously these occurrences cannot be evaluated by conventional techniques, and only a few sites in the sheared serpentine have been outlined as ore bodies. At least 100 million tons of flaky material amenable to processing occurs in masses of proportions suitable for mining. Conceivably, resources totaling several times this amount could occur in this 14-mile serpentinite mass. In nearby localities other serpentinite masses rather similar in character remain to be prospected. Obviously this is a significant resource, but of Group 7 fiber only, and it will long be the prime source for certain California asbestos fabrication plants and may ultimately supply a much expanded industry. Because these resources are not typical of the content of fibers, and cannot be put to the wider range of uses represented in asbestos resources tabulated for other districts, they are not included in the foregoing tabulation of conventional asbestos resources available in the United States.

Of more than 90 asbestos prospects reported in the serpentinites of California at least half are chrysotile occurrences (Wiebelt and Smith, 1959). About 30 are tremolite or anthophyllite occurrences. Intermittently, small tonnages of weak fiber that has limited use have been mined from some of the amphibole deposits, and occurrences of this type that remain cannot be expected individually to have more potential, in either volume or quality. Most of the little-known prospects for which the mineral species is not reported are likely mere mineralogic occurrences. Geologic settings with promise of hosting extensive chrysotile stockworks of the Quebec type are most numerous along the western foothills of the Sierra Nevada and in the Klamath Mountains, which is a northern outlier of the foothills belt. Among or in the vicinity of the chrysotile prospects of these areas, it is reasonable to anticipate that at least a few and perhaps several additional deposits comparable to the Copperopolis ore body will ultimately be discovered. The possibility of large stockworks of chrysotile in the serpentinite masses west of the Great Valley of California is certainly not to be overlooked, but relatively few of these appear—from sparse information—to be promising in their geologic settings.

In east-central Oregon, along the presumed offset continuation of the Pacific Coast ultramfic belt, exposures of serpentinite masses are sparse compared to the numbers and volume exposed in the California interval. Oregon is thus a less promising region to prospect. The most promising known eastern Oregon chrysotile occurrence has been explored by modern techniques, apparently without outlining significant amounts of asbestos.

Other domestic occurrences of chrysotile in massive serpentinite receive intermittent attention as possible targets for prospecting. Most noteworthy among these are occurrences at various localities near the Kobuk River in northwestern Alaska (Bowles, 1955, p. 17) and scattered prospects in Wyoming opened during and before World War I (Beckwith, 1939). Past prospecting of the northwest Alaska occurrences was directed mainly toward determining mineral species and whether fibers of textile length existed. Most of the prospected occurrences are of short-fiber chrysotile; data available provide little hint as to whether or not any are potential targets for outlining extensive deposits.

In the area prospected for chrysotile a few miles south of Casper, Wyo., rocks other than serpentinite make up the bulk of exposures; many of the serpentinite exposures are barren of asbestos, and apparently none exhibit faces extensively veined by asbestos. It is not certain that any of these serpentine masses are large enough to contain an asbestos deposit of minable size. Serpentine masses south of Lander, Wyo., are moderately well exposed and obviously large enough to include minable stockworks of chrysotile; none of the present exposures contain enough asbestos to encourage mining, but chrysotile veining is widespread enough to suggest that the occurrence could be reassessed as a possible target for exploration by modern techniques.

The chrysotile resources of Arizona are entirely in deposits of the limestone type. At any given time, reserves estimated for the entire district aggregate only a few thousand tons. From considerations of geologic habit and regional distribution, an estimated 75,000 to 100,000 tons of fiber remains to be discovered within the depths at which these typically small deposits can be economically mined (Shride, 1969). Those resources include a high proportion of long fiber. When available, as in the past, these resources will largely be marketed only for special uses. Chrysotile occurrences of the Arizona type known in the Panamint Mountains of eastern California and near Cliff Lake in the Madison Range of southwestern Montana are erratic in fiber distribution. They do not approach the Arizona deposits in quality of fibers or in continuity of the mineralized zones and cannot be regarded as recoverable resources.

MEXICO

The search for and mining of chrysotile asbestos

is just beginning in Mexico. Two widely separated deposits contain the reported reserves. Until more is known of the settings of these occurrences, geologic projection of additional resources is not plausible. The expanding asbestos-cement product industry of Mexico will long have first call on any resources that can be discovered in that country.

PROSPECTING TECHNIQUES

Quebec-type chrysotile deposits are large enough targets to be searched out by geophysical techniques; the magnetite ubiquitous in ultramfic terranes determines the prospecting method. Magnetite, most abundant in parts of the ultramfic complexes most intensely faulted, is thus a common constituent of asbestos veins and adjacent wallrock, where anomalous concentrations can be outlined by magnetic surveys. Major zones of shearing and bodies of serpentinized dunite, both likely to be barren of asbestos, can also be expected to exhibit strong magnetic anomalies. Therefore, interpretation of magnetic data is most effective when done with knowledge of the geologic habits of the ultramafics of a given area. Ground surveys have long been a prime method to outline potential asbestos-bearing zones (Low, 1951). Airborne magnetic surveys are especially effective for reconnaissance to locate serpentinite masses, and with moderate geologic ground control or local supplementation by ground magnetic surveys, airborne surveys can be used to outline geologic features of possible economic significance (Conn, 1970).

PROBLEMS FOR RESEARCH

The reasons for the restriction of large concentrations of chrysotile asbestos to certain very limited intervals in an alpine-type serpentine belt are not yet clear. Data of the sort that led to the recent recognition (Irwin, 1964) that serpentinites of the Klamath Mountains of northern California are somewhat older (and the subjects of a different tectonic history) than serpentinites contiguous to the west are possibly the kind of field data needed for future evaluations. In this instance the known chrysotile occurrences may be entirely restricted to the older serpentinites.

The evolution of ideas on the tectonic emplacement of alpine-type serpentinites should be given close future attention for hints as to targets for asbestos exploration. The restriction of asbestos concentrations to only parts of the geosynclinal belts may be related to a certain sequence of structural events, or to optimum pressures or temperatures operative in one tectonic wedge and not in an adjacent mass. Appraisals are being made of the strength and ductility or brittle behavior characteristics of the various serpentinites. Certainly the degree of competence prevailing at the time when energy and solutions were available for the late (local) stage serpentinization was a vital factor in formation of a minable deposit. As a part of the "global tectonics" research, physical properties of the various occurrences of serpentinite may one day be accurately and readily defined; these data and the techniques used in their determination should be given attention for practical application. As a potential secondary result of such studies, for instance, perhaps magnetic anomalies directly related to asbestos localization may be differentiated from magnetic phenomena that are not so related.

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BARITE

By Donald A. Brobst

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ABSTRACT OF CONCLUSIONS

The world production of barite ($BaSO_4$, barium sulfate) has increased from less than 1.5 million tons in 1945 to more than 4 million tons in 1970. The world's estimated total barite production from 1850 to 1971 amounted to nearly 92 million tons, but nearly 75 percent of that total was mined between 1945 and 1971 and increasing use is forecast, particularly inasmuch as barite is vital to the petroleum industry, which in 1972 consumed 80 percent of the world's annual production. The United States is self-sufficient and should remain so, even with modestly increasing demands placed on its resources.

Three major types of barite deposits are vein and cavity-filling, residual, and bedded deposits. The vein and cavity-filling deposits of the world constitute large resources of barite, much of which are recoverable as byproducts or coproducts. Residual deposits at shallow depths constitute a large resource in the United States. Bedded deposits of fetid black fine-grained barite, commonly of high grade (50–95 percent barite), are abundant in siliceous sedimentary rocks of mid-Paleozoic age. The bedded deposits, probably of sedimentary origin, are a large part of the barite resources of the United States. Similar large deposits probably lie undiscovered in many parts of the world.

The total of the world's barite resources in all categories is about 2 billion metric tons of barite, but only about 300 million metric tons (15 percent) are identified resources, which are the sum of currently minable ore (reserves) and lower grade material of subeconomic value now (conditional resources). If future industrial demands are to be met, hypothetical and speculative resources will have to be converted to identified resources, and this will require continued geological research on barite and barium minerals.

INTRODUCTION

Barite ($BaSO_4$, barium sulfate) is extremely vital to the petroleum industry, which consumes much of the world's current annual production of about 4 million tons, as a major ingredient of the heavy fluid, called mud, that is circulated in the rotary drilling of oil and gas wells. Barite also is a source for various barium compounds and barium metal whose uses also are nearly hidden among the technical complexities of modern industrial processes and products.

In the United States, about 80 percent of the 1.5 million tons of barite consumed annually is ground finely (90 percent, minus 325 mesh) for use in drilling mud, the circulation of which lubricates the drill stem, cools the drill bit, seals off the walls of the hole, removes cuttings, and confines the high oil and gas pressures met at depth. The latter feature aids in the prevention of gushers, thus reducing

waste of oil and gas resources and environmental pollution, as well as conserving the natural pressure for greater production and rate of recovery of the products in the reservoir rocks. Barite is particularly well suited for drilling mud because it is soft, heavy, chemically inert, and available in sufficient quantity at competitive prices throughout much of the world. Many heavy materials tried as substitutes for barite in drilling mud have been rejected simply because of excessive initial cost, because they react chemically in the system, or because they abrade pipes, pumps, and hole walls resulting in increased drilling costs.

The remaining 20 percent of barite consumed annually in the United States goes chiefly into the manufacture of glass to add brilliance and clarity; into the wares of the paint and rubber industry principally as a pigment and filler; and into the chemical industry for the preparation of barium compounds. Barite is a common industrial filler, extender, and weighting agent. A survey of the uses of barium chemicals by the Food Machinery and Chemical Corp. (1961) listed more than 2,000 specific industrial applications in 17 major classifications. Among the newer developments are the use of barium titanate ceramics in the electronics industry and of barium ferrate ceramics in permanent magnets. Barite, a good absorber of gamma radiations, has been used as an aggregate in concrete for shielding in atomic reactors, thereby reducing the amount of more expensive lead shielding otherwise needed.

With energy requirements rising in the United States and throughout the world, there is every reason to believe that demand for mud-grade barite (92–94 percent $BaSO_4$) will continue at high levels, and even increase, as the search for oil and gas continues. Not only will more wells be drilled, but they will be deeper and they will extend into high-pressure reservoirs requiring the use of more barite as the potential for blowouts and mud leakage increases. Other industrial uses of barite are sure to continue at accelerated rates as the population grows, as new nations industrialize, and as economies expand in the older industrial nations. Further information on uses, material specifications, economics, production, and outlook for future demand of barite has been given recently by Brobst (1970) and Lewis (1970).

As the decade of the 1960's closed, nearly 1 million tons of barite was produced annually in the United States, chiefly in Missouri, Arkansas, Nevada, Georgia, and Tennessee. Another half million tons was imported annually from various countries, especially Canada, Mexico, Peru, Ireland, Greece, Yugoslavia, and Morocco. Current knowledge of the widely distributed domestic reserves of barite suggests that the United States could be self-sufficient in barite for some years, even at moderately increasing rates of consumption (Brobst, 1970, p. 11–12).

EXPLOITATION

Commercial demand for barite began about mid-19th century when the United States and the nations of western Europe began to industrialize. Estimates of the world's barite production compiled from various sources are shown in table 12. Nearly 75 percent of the total world's barite production of nearly 92 million tons has been mined since 1945, and the United States has consumed 46 million tons (about half) of this amount.

TABLE 12.—*Barite, world production and U.S. production and imports, in millions of short tons, 1850–71.*

[Compiled from U.S. Bur. Mines data and many other sources]

	World production	U.S. production	U.S. imports
1850–1914	[1] 6.5	1.2	0.2
1915–18	1.2	.7	[2] 0
1919–44	16.7	7.1	.9
1945–71	67.5	23.5	12.5
Total	91.9	32.5	13.6

[1] Author's estimate: few foreign production data available.
[2] 2,500 short tons imported during this period.

Figure 10 shows world production, U.S. production, and U.S. consumption (production plus imports) from 1919 to 1971. The three curves are almost parallel until 1959, after which barite consumption outside of the United States increased sharply because of an expanding world need for mud-grade barite. The peak between 1925 and 1930 coincides with the period when barite was first used for drilling mud.

From 1838 to 1971, the residual deposits of the United States have yielded about 17 million tons of barite, the bedded deposits about 11.5 million tons, and the vein deposits about 4 million tons. Before 1940, most of the U.S. barite production came from residual deposits, chiefly in Missouri, Tennessee, and Georgia. After 1940, the black bedded barite deposits of Arkansas came into production and within a few years the barite produced rivaled, and in some years exceeded, that of the great residual deposits of Missouri. The bedded deposits of Nevada have been worked since early in the 20th Century at rates that since 1960 have increased almost annually.

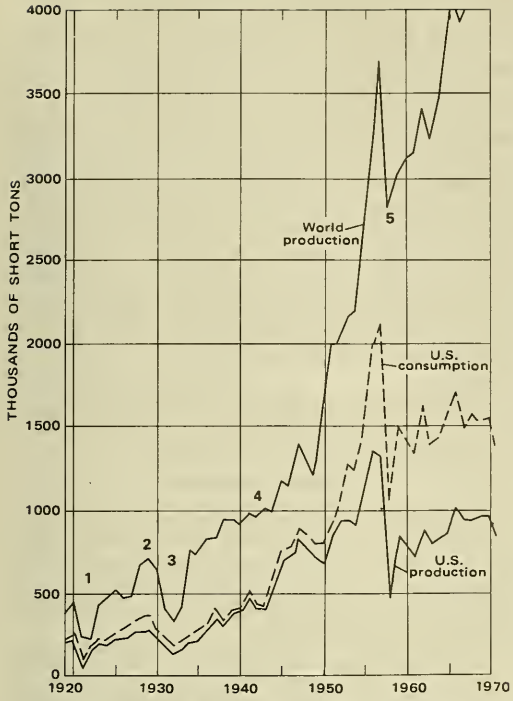

FIGURE 10.—Barite, world production and U.S. production and consumption, 1919–71. 1. Post-World War I depression. 2. Barite drilling mud introduced and accepted. 3. Economic depression. 4. World War II. 5. World economic recession.

Barite has been or could be produced as a by-product or coproduct of some fluorspar, base and precious metal, and rare-earth deposits. These sources of barite have not been greatly utilized for many reasons. Some deposits are too far from markets, or the additional milling operation cannot be handled by existing mills. The barite is too irregularly disseminated in some deposits, and the demand for the major product too variable to guarantee the barite user a steady supply in others. Economic changes may bring much of this barite into future markets.

Most of the barite mined in the United States has been mined in open pits. The mining of residual deposits has brought on the need to rehabilitate many acres of worked ground. In many areas of shallow residual deposits, rehabilitation is not difficult, but any costs will ultimately be paid by the consumer.

GEOCHEMISTRY

Recent estimates of the abundance of barium in the earth's crust (Parker, 1967; Lee and Yao, 1970) suggest that the value lies in the range of 300–500 ppm (parts per million equals grams per metric ton; 1 ppm equals 0.0001 percent). In igneous rocks, the basalts contain as little as 100 ppm Ba; granites commonly contain 700–800 ppm Ba; syenites and some of the more potassic igneous rocks contain as much as 3,000–5,000 ppm Ba. The role of barium in the crystallization of igneous rocks has been discussed by Dunham and Hanor (1967). Among the sedimentary rocks, shale generally contains the most barium (500–1,000 ppm) and limestone contains the least (commonly less than 200 ppm). The barium content of sandstone varies widely, from a few to several hundred parts per million.

The large size of the barium ion in its common valence state (Ba^{+2}, 1.43 angstrom units) makes isomorphous substitution possible only with strontium (Sr^{+2}, 1.27) and generally not with the other members of the elements of Group 2A of the periodic table (Ca^{+2}, 1.06; Mg^{+2}, 0.78). Among the other elements that occur with barium in nature, substitution is common only with potassium (K^{+}, 1.33), but not with the smaller ions of Na, Fe, Mn, Al, and Si in their most common valence states. This explains why the potassium-rich igneous rocks contain the greatest amounts of barium. The barium commonly substitutes for potassium in the minerals of the feldspar and mica groups.

Unlike many other common metals, the sulfide of barium is water soluble, the sulfate is virtually insoluble in distilled water, and, as the chloride the element is easily transportable. Barium, therefore, is mobilized, transported, and concentrated under different conditions from those which govern the course of many base and ferrous metals in the geochemical cycle.

The geochemical cycle of barium begins with its arrival in the upper crust of the earth as a result of volcanic activity and the emplacement of intrusive igneous rocks and any attendant vein systems. The mechanical and chemical disintegration of igneous rocks releases barium to the sedimentary cycle through which it is carried seaward as fine particles of mineral material, or as ions absorbed on particles of clay size, or perhaps attached to negatively charged sols, such as $Mn(OH)_4$. In the sea, ionic barium will combine readily with available sulfate anions to form a precipitate of barium

sulfate (barite), which accounts for the low concentration of barium in sea water.

Connate brines of many sedimentary formations contain barium chloride ($BaCl_2$) which on mixing with sulfate-rich waters will yield a precipitate of barite. This process has caused problems in oil field operations, notably in the Wilmington (Long Beach, Calif.) oil field (Gates and Caraway, 1967).

The geochemistry of barium is complex. More information and many references are available in the works of Rankama and Sahama (1950), Graf (1960), and Friedman (1969).

ORE MINERALS OF BARIUM

Barite, the chief ore mineral of barium, when pure, has a specific gravity of 4.5, has a hardness of 3 on Mohs' scale (in which the hardness of a fingernail is about 1.5), and contains 58.8 percent barium and 41.2 percent sulfate. The mineral occurs in assorted colors, although shades of white to dark gray and black are common in commercial deposits. Barite crystallizes in the orthorhombic system and commonly forms prismatic or tabular crystals. Generally it is found in irregular masses, concretions, nodules, rosettelike aggregates, and in massive to laminated beds. Mine-run ores contain some inclusions and intergrowths of other minerals as well as small amounts of other elements (Brobst, 1958, p. 80–81). Barite of vein and residual deposits commonly contains several percent strontium.

Barite is most commonly associated with quartz, chert, jasperoid; calcite, dolomite, siderite, rhodochrosite, celestite; fluorite; and various sulfide minerals, such as pyrite, chalcopyrite, galena, sphalerite, and their oxidation products. Ferruginous clays make up a large part of residual deposits of barite. Barite is a common gangue mineral in many types of ore deposits, especially in veins that are mined principally for other commodities, including lead, zinc, gold, silver, fluorite, and rare-earth minerals. Barite is a common constituent of some siderite-rich iron deposits in Europe, but deposits of this type have not been found in the United States.

Witherite ($BaCO_3$, barium carbonate, 69.6 percent Ba and 30.4 percent CO_3), a highly desirable source for the production of barium chemicals because of its solubility in hydrochloric acid, occurs as a minor accessory mineral in some barite deposits. Like barite, this mineral also crystallizes in the dipyramidal class of the orthorhombic system. Witherite has a hardness of 3–3.5 on Mohs' scale and a calculated specific gravity of 4.29. In the United States, only the El Portal mine, Mariposa County, Calif., has produced witherite in large amounts; operations ended there about 1950. Nearly all the world's supply of witherite in 1972 came from the Settlingstones mine, Northumberlandshire, England. Witherite is probably only a very small part of the barium resources of the world.

Sanbornite ($BaSi_2O_5$), which contains 50 percent barium, is of potential interest as a source of barium for chemicals because, unlike many silicate minerals, it is soluble in acid. The solubility permits the recovery of the barium by further chemical processing. The mineral, formerly considered rare, has been found in abundance associated with other barium silicate minerals in contact with metamorphic rocks, mostly quartzite, in roof pendants of the Sierra Nevada batholith in Fresno County, Calif. (Matthews and Alfors, 1962). The resource potential of sanbornite deposits is virtually unstudied.

Barium occurs in other minerals, but in concentrations so low that none of the minerals are likely to be potential sources of the element.

TYPE OF DEPOSITS

Barite occurs in many geological environments in sedimentary, igneous, and metamorphic rocks. The geologic relations of three major types of commercial deposits, the vein and cavity-filling, the residual, and the bedded deposits, have been summarized by Brobst (1958).

Some recent references to the geology of barite are given in this report; others are available in an annotated bibliography by Dean and Brobst (1955), and in a pamphlet included with a map (at a scale of 50 miles to the inch) which shows the size and distribution of deposits in the United States (Brobst, 1965). A summary of the geology and reserves of barite deposits of the world (Brobst, 1970) also includes a bibliography of about 100 references to deposits outside the United States.

VEIN AND CAVITY-FILLING DEPOSITS

The vein and cavity-filling deposits are those in which barite and associated minerals occur along faults, gashes, joints, bedding planes, breccia zones, and solution channels and in various sink structures. The deposits in solution-channel and sink structures are most common in limestone. The host rocks are of Precambrian to Tertiary age in the United States. Many deposits in the Western States are associated with igneous rocks of Tertiary age, although notable exceptions are vein deposits of barite and rare-earth minerals associated with igneous rocks of Precambrian age at Mountain Pass, San Bernardino County, Calif., and in the Wet Mountains,

Custer County, Colo. In most of the deposits in the Eastern and Midwestern States an association with igneous activity is not obvious.

Most of the barite in veins and cavity fillings is dense and gray to white, and is associated with many other minerals including the minerals of the metallic ores as already mentioned. The grade of the barite ore varies by deposit and within deposits. The deposits commonly have sharp contacts with wallrocks; large-scale replacement of the host rocks by vein minerals is rare. Within individual districts, the deposits commonly are scattered and irregular, and range in thickness from a few inches to a few feet and in length from tens to hundreds of feet. Barite cementing of breccia along fault zones forms thin deposits of small extent in the eastern United States. On weathering, fault-breccia deposits may form bodies of residual ore.

Barite deposits in collapse and sink structures are common in central Missouri where they are known as circle deposits, and in the Appalachian States. The deposits have yielded rich ore but the individual bodies tend to be small. On weathering, these deposits also form valuable bodies of residual ore.

The barite and other minerals of the vein and cavity-filling deposits are typical of an epithermal suite precipitated from low-temperature solutions. Many geologists agree that most vein deposits containing barite in the Western States had such an origin. A hydrothermal origin also is postulated for many deposits in the midcontinent region and in the Eastern States where the term "telethermal" has been applied to indicate that the solutions traveled farther from their source, and therefore, were somewhat cooler than those generally termed "epithermal." Evidence has been accumulating in the past decade to suggest that some barite and minerals of base metals may form vein deposits from circulating ground waters (meteoric or supergene water).

RESIDUAL DEPOSITS

Residual barite deposits in unconsolidated material are formed by weathering from preexisting deposits. Many residual deposits of commercial interest lie within the clayey residuum derived from Cambrian and Ordovician limestone and dolomite, especially in southeastern Missouri (Brobst and Wagner, 1967) and the Appalachian region (Brobst and Hobbs, 1968). These include deposits in the major barite districts at Sweetwater, Tenn. (Maher, 1970, p. 13) and Cartersville, Ga. (Kesler, 1950), and many lesser known districts in Alabama and Virginia.

Most residual barite is white and is translucent to opaque; it occurs in discrete mammillary, fibrous, platy, or dense fine-grained irregular masses most of which range in longest dimension from about 1 to 6 inches. Small amounts of pyrite, galena, and sphalerite occur in or on some of the barite, and locally some lead and zinc may be minor by-products of barite mining. Chert and jasperoid are common in many deposits. Incompletely weathered rock fragments, and red, yellow, or brown clay typically make up the rest of most deposits.

The grade of the ores varies greatly, but commercial mining now requires a minimum of about 220 pounds of recoverable barite per cubic yard of residuum. Much of the typical ore in major districts has 200–300 pounds of recoverable barite per cubic yard of residuum.

Deposits in Washington County, Mo., are in residuum overlying bedrock 10–15 feet below the surface. The deposits at Cartersville, Ga., are in residuum that is as deep as 150 feet. Commercial deposits are commonly many acres in extent, but the shape of the residual deposit depends on the shape of the original deposit. Deposits derived from solution channels and vein systems tend to be elongate, and those derived from sink structures tend to be circular.

Ribs or pillars of carbonate bedrock protrude upward into the residuum at many deposits. Some of the ribs contain veins filled with barite, fluorite, quartz, calcite, and locally some sulfide minerals including pyrite, chalcopyrite, galena, and sphalerite. In other deposits, only thin veinlets or disseminated lumps and pods of barite occur in the carbonate bedrock. The source of the barite in residual deposits generally has been assumed to be epigenetic (introduced) hydrothermal vein material left after the host rock has been chemically destroyed.

Today's knowledge of mineralogy and crystallography suggests that any barium that was trapped in precipitating carbonate will fit into the lattice of aragonite, which seems to be a common primary precipitate of calcium carbonate. Because of the differences in ionic radii of the cations and the crystal structure, barium will not fit into the lattice of calcite or dolomite. Thus, when aragonite is converted to calcite or dolomite, any structurally included barium is expelled from the lattice. It seems reasonable to suppose that any sulfate present in the pore fluids might then fix the barium as barite in veinlets or nodules in the carbonate rocks. If the pore fluid is chloride-rich, and sulfate-poor, the expelled barium might be converted to the very

soluble chloride, in which case the barium could be held in solution to be precipitated later, in place or elsewhere, as barite when sulfate ions became available. Connate water may play an important role in the redistribution of barium in the carbonate environment. The foregoing is perhaps an oversimplification of a complex chemical process, but it does offer an explanation of why calcite- and dolomite-rich rocks generally contain such small amounts of barium. Just as important perhaps is the largely unevaluated role of organisms, especially bacteria, in the mobilization and redistribution of elements such as barium in the sedimentary environment under conditions of low temperature and pressure.

BEDDED DEPOSITS

Bedded deposits include those in which barite occurs as a principal mineral or cementing agent in stratiform bodies in layered sequences of rock. The major deposits of commercial value in this group are bedded concentrations of fetid dark-gray to black fine-grained barite, some of which contain millions of tons of barite easily beneficiated for use in drilling mud and chemical plants. Deposits were being mined in 1972 in Arkansas, California, and Nevada. Geological details are available for some deposits in Arkansas, including the major deposit at Magnet Cove (Scull, 1958; Zimmermann and Amstutz, 1964); in Nevada, including deposits in the Toquima Range (Shawe and others, 1969) and the Shoshone Range (Ketner, 1965; Zimmermann, 1969); and in California, near Castella, Shasta County (Weber and Matthews, 1967). The bedded deposits and their origin are discussed in some detail here because of the economic value of these deposits and the good potential for finding more of them in many parts of the world.

Geologic features of the bedded deposits may be summarized briefly. The dark beds of barite are a few inches to 50 feet thick and extend over many acres. The beds commonly occur interbedded with dark chert and siliceous siltstone and shale. Some ore zones are more than 100 feet thick. Some individual beds of barite are massive, but more commonly the beds are laminated. The grains of barite generally are less than 0.1 mm in diameter. Barite nodules and rosettes make up a substantial part of some barite beds, and a smaller part of some silty or shaly beds. Some nodules have concentric rings of barite, and the rosettes have a radially bladed structure. Both structures suggest that room for free growth existed during deposition. Conglomeratic beds consisting of nodules and fragments of barite, chert, phosphate (apatite), and fragments of rock in a fine-grained matrix of barite have been found in the Toquima Range, Nev. (Shawe and others, 1969, p. 248). Many small-scale sedimentary textures and structures, as well as rhythmic alternations of beds have been described (Zimmermann and Amstutz, 1964; Zimmermann, 1969).

Many beds of ore in these deposits consist of 50–95 percent barite. The chief impurity is fine-grained quartz whose abundance is inverse to that of barite. Small amounts of clay and pyrite are common. Carbonate minerals are rare. Spectrographic analyses of many samples indicate that the environment of these barite deposits is extremely low in calcium and magnesium—the total of these two elements generally is less than 1 percent. The most abundant minor element is strontium; it occurs in amounts up to about 7,000 ppm. The trace element suite is limited, and the abundance of each element is unusually small as compared with the suite and abundance of the trace elements in vein deposits. Manganese and vanadium generally are each less than 50 ppm. Cobalt, copper, chromium, nickel, yttrium, and zirconium each are less than 20 ppm.

The beds of black bedded barite contain several percent organic matter and characteristically give off the odor of hydrogen sulfide (H_2S) when struck with a hammer. The hydrogen sulfide is believed to be the product of the decay of organic matter and reduction of sulfate by anaerobic bacteria. Fatty acids, hydrocarbons, and other organic compounds (a geolipid fraction) have been extracted from samples collected in Arkansas, California, and Nevada (Miller and others, 1972). The fatty acids identified are considered to be biological markers for the cell walls of bacteria that probably once lived on or within the crystallizing barite masses.

Rocks containing the black bedded deposits commonly are of mid-Paleozoic age even though they are widely scattered geographically. The relation is not fully understood, but is perhaps more than coincidental. Most of the deposits in Arkansas are of Devonian and Mississippian age; those in California and Nevada are mostly of Devonian age, although some in Nevada may be of Ordovician age. Somewhat similar deposits at Meggen, Westphalia (Ehrenberg and others, 1954), and in the Saarland (Krebs, 1970) of western Germany also occur in Devonian rocks.

Earlier workers have proposed that the black fetid beds of barite in Arkansas (Scull, 1958) and Nevada (Ketner, 1965) originated by replacement of carbonate rocks by barium-bearing hydrothermal solutions stemming from intrusive igneous activity.

The appeal of this hypothesis is greatly reduced by (1) the absence of igneous rocks in the vicinity of many deposits, especially in western Arkansas, except for the Magnet Cove deposit; (2) the absence of anomalously large concentrations of such elements as copper, lead, zinc, silver, molybdenum, and mercury expected in and around hydrothermal ore deposits; and (3) the absence of abundant carbonate rock available for replacement in the formations that contain rich beds of barite.

The black bedded barite deposits probably are of sedimentary origin, formed virtually at the same time as the enclosing rocks by organic and inorganic chemical processes of concentration and deposition. A sedimentary origin for the deposit at Magnet Cove, Ark., was postulated by Zimmermann and Amstutz (1964) from structural and textural evidence. Zimmermann (1969) later found similar features in the deposits of the Shoshone Range, Nev. Shawe, Poole, and Brobst (1969) proposed a sedimentary origin for the deposits in the Toquima Range, Nev., because of textural, structural, and chemical features, including the effects of contact metamorphism on the barite beds (coarsening of the grain size by recrystallization and bleaching of the dark color) from the emplacement of an igneous rock.

The source of the barium in these deposits has not been established, although some hypotheses have been proposed. Sources in submarine volcanic emanations and springs were suggested for the barite and sulfide beds at Meggen, Germany (Ehrenberg and others, 1954). Hydrothermal solutions are considered by Dunham and Hanor (1967) to be the ultimate source of all barite deposits. A barium source in sea water, with extraction related to biological activity, was discussed by Shawe, Poole, and Brobst (1969).

The recycling of barium from preexisting rocks should not be overlooked as a source of barium for these bedded deposits. Connate brines seem to be good concentrators and transporters of barium, as already observed in the discussion of residual deposits. Barium-rich chloride waters reaching sulfate-rich marine or brackish water could mix locally to yield deposits of barite. If this mechanism functions in nature, the possibility of finding barite deposits at the sites of ancient or modern lakes and swamps containing sufficient sulfate, especially in coastal areas, must be considered seriously.

White to clear barite occurs as a cement in some sandstones and conglomerates, such as the Pike Gravel, the basal formation of the Trinity Group of Cretaceous age in Howard and Sevier Counties, Ark. (Scull, 1958). The Pike Gravel marks the Cretaceous strandline and unconformably overlies folded rocks of Paleozoic age. About 20 miles to the north, the Paleozoic rocks contain deposits of black bedded barite, which perhaps are the source of the barium for the barite cement in the Pike Gravel.

RESOURCES

IDENTIFIED AND HYPOTHETICAL RESOURCES

The identified and hypothetical resources of barite in the United States are listed by State and type of deposit in table 13. The identified resources include

TABLE 13.—*Identified and hypothetical barite resources of the United States, in thousands of short tons*

[+, indicates present in small, but otherwise unknown, amounts]

	Identified resources [1]			Hypothetical resources [2]		
	Bedded	Residual	Vein	Bedded	Residual	Vein
Alaska	----	----	5,000	----	----	10,000
Washington	500	----	100	1,000	----	500
Idaho	500	----	100	1,000	----	500
Montana	----	----	500	----	----	1,000
California	1,000	----	5,000	5,000	----	25,000
Nevada	35,000	----	1,000	50,000	----	1,000
Arizona	----	----	1,000	----	----	1,000
New Mexico	----	----	100	----	----	100
Utah	----	----	100	----	----	100
Colorado	----	----	500	----	----	1,000
Oklahoma	----	25	----	----	50	----
Texas	----	----	100	----	----	100
Wisconsin	----	----	5,000	----	----	1,000
Missouri	----	15,000	500	----	5,000	2,000
Arkansas	10,000	----	----	5,000	----	----
Illinois	----	----	5,000	----	----	5,000
Kentucky	----	+	5,500	----	+	6,000
Tennessee	----	3,000	1,000	----	6,500	15,000
Alabama	----	25	----	----	500	----
Georgia	----	2,000	----	----	5,000	----
South Carolina	----	----	1,000	----	----	2,000
North Carolina	----	----	200	----	----	1,000
Virginia	----	25	----	----	500	----
Maryland	----	+	5	----	5	5
Pennsylvania	----	+	5	----	5	----
Connecticut	----	----	----	----	----	500
Sub total (rounded)	47,000	20,000	31,700	62,000	17,500	72,800
Total, all types (rounded)	----	----	99,000	----	----	152,000

[1] Identified resources: Specific, identified mineral deposits that may or may not be evaluated as to extent and grade, and whose contained minerals may or may not be profitably recoverable with existing technology and economic conditions.

[2] Hypothetical resources: Undiscovered mineral deposits, whether of recoverable or subeconomic grade, that are geologically predictable as existing in known districts.

currently minable ore (reserves) and lower grade material of subeconomic value (conditional resources).

Deposits of bedded barite in the identified resources include those within 500 feet of the surface whose ore contains at least 40 percent barite. Ores containing 40 to about 92 percent must be beneficiated to yield a product for drilling mud. Flotation techniques for concentrating these ores are in common use. Selective mining in many of the deposits yields substantial tonnages of barite that requires only grinding for use as drilling mud.

Estimates of the identified resources of barite in residual deposits include materials to a depth of

250 feet (most are much shallower) that contain more than 125 pounds of recoverable barite per cubic yard of residuum processed. This cutoff includes material that is subeconomic by the 1972 standards of about 220 pounds of barite per cubic yard of residuum. An identified resource of 1.9 million tons of barite is reported in 67 tailings ponds in the Washington County barite district, Missouri (Wharton, 1972, p. 55).

Identified resources of vein material include ores in a wide variety of grades, with and without potential coproducts in deposits within 1,500 feet of the surface. The common coproducts are, or could be, one or more of the following: fluorspar and minerals of lead, zinc, silver, gold, and rare earths. Some of these barite ores must be literally rediscovered in known metal districts. In earlier times, bodies of mixed ore, especially of barite and fluorspar, were bypassed in mining because it was then impossible to beneficiate them economically. Techniques for the beneficiation of these mixed ores are now available. The estimates of resources also include some barite available by reprocessing mine dumps and tailings ponds. Parts of settling ponds at old washer plants in the Washington County district, Missouri contain as much as 35 percent fine-grained barite.

Barite resources of Alaska have scarcely been evaluated, but are of considerable interest because of anticipated oil production on the Arctic slope. Vein deposits were mined in 1972 on Castle Island in the Petersburg region, and vein deposits in the Skagway area have been recently described by MacKevett (1971). A potential ore target for barite, fluorite, and metal sulfides has been identified near Nome on the Seward Peninsula (Brobst and others, 1971). In northern Alaska, gray barite occurs in cherty rocks of Paleozoic age (Tailleur, 1970), and abundant barium occurs in shales of Mesozoic age that are rich in organic matter (Tourtelot and Tailleur, 1965). The distribution of the occurrences suggests that the Brooks Range might also contain barite deposits of commercial value.

Hypothetical resources listed in table 13 were estimated for each type of deposit using the same limiting depth as for the identified resources; however, the cutoff for bedded deposits is reduced to 30 percent barite and for residual deposits to 75 pounds of recoverable barite per cubic yard of residuum processed. The grade of vein deposits included in this estimate varies as widely as in identified resources, but a favorable potential for coproducts is regarded as economically necessary for exploitation.

A summary of the world's identified and hypothetical resources of barite is shown by continent in table 14. The identified resources are extrapolated

TABLE 14.—*World resources of barite in millions of metric tons*

Area	Identified [1]	Hypothetical [2]	Speculative [3]
North America	118	180	400
Central America and the West Indies	2	5	10
South America	15	20	100
Europe	75	85	220
Africa	38	50	200
Asia	52	50	300
Oceania	10	10	50
Totals	310	400	1,280

[1] Identified resources: Specific, identified mineral deposits that may or may not be evaluated as to extent and grade, and whose contained minerals may or may not be profitably recoverable with existing technology and economic conditions.
[2] Hypothetical resources: Undiscovered mineral deposits, whether of recoverable or subeconomic grade, that are geologically predictable as existing in known districts.
[3] Speculative resources: Undiscovered mineral deposits, whether of recoverable or subeconomic grade, that may exist in unknown districts or in unrecognized or unconventional form.

from world reserve data described and tabulated by Brobst (1970). Outside the United States, perhaps as much as 75 percent of the identified barite resources are in vein deposits, many of which are mined or are minable for multiproducts. The hypothetical resources are predicated on estimates for similar types of deposits in the United States.

Barium-rich nodules have been found on great areas of the sea floor. The barite might eventually be recovered as a coproduct with other materials, notably manganese, although much remains to be done on the recovery and processing techniques. The resources probably are large, but they are as yet mostly unmeasured, and none are included in the total for identified resources of conventional deposits.

Barite is associated with carbonatite in east Africa and probably elsewhere in the world, but the commercial potential of these deposits remains to be evaluated fully.

In northern Honshu, Japan, layered volcanic rocks of Miocene age contain black ore (kuroko) consisting of economically recoverable amounts of pyrite, barite, copper, lead, zinc, silver, and gold. The geology and beneficiation of these ores have been described recently (Mining Engineering, 1969). Deposits similar to these also might occur in the Western United States and other countries in the circumpacific volcanic belt. Deposits of this type probably have not been sought in many places where potential for their discovery is good.

SPECULATIVE RESOURCES

The speculative resources, those of undiscovered districts, are large.

It is highly probable that additional deposits of black bedded barite will be found in dark siliceous

sequences of sedimentary rock of Paleozoic age in Arkansas, Nevada, and California. Some bedded deposits also might occur in the Ouachita Mountains of eastern Oklahoma. The potential for the discovery of bedded deposits of value in Alaska is great. The Appalachian region probably has never been explored for bedded deposits. The bedded deposits tend to be large but are easily overlooked. They are worthy targets for exploration in sedimentary rocks throughout the world.

Undiscovered deposits of considerable size probably occur in the Appalachian region from Pennsylvania to Alabama in the residuum of Cambrian or Ordovician carbonate rocks. Additional districts the size of the Sweetwater district, Tennessee, and the Cartersville district, Georgia, probably are hidden in the region. Other new districts containing residual deposits of barite may be found in the midcontinent region in the residual mantles on barite-bearing rocks.

The speculative resources of barite in vein deposits are large. Much barite will become available as a coproduct from base-metal, rare-earth, and fluorspar veins. Discovery of at least one other fluorspar district containing large amounts in the midcontinental United States and similar to the Illinois-Kentucky district seems probable. The discovery of additional rare-earth and barite deposits such as those in the Mountain Pass district, California, also is probable.

The caprock and environs of the salt domes in the coastal areas of the Gulf of Mexico and other regions of the world might contain barite deposits. Abundant chloride and sulfate ions in connate waters in this environment enhance the possibilities for concentration of barite there.

The world's speculative resources of barite are listed in table 14. Speculative resources of the United States are estimated to be about 250 million metric tons (1 short ton equals 0.91 metric ton) as compared with 400 million metric tons of barite for all North America. Speculative resources for Europe and North America are proportionally smaller as compared to their identified and hypothetical resources than are those for other regions of the world, because more intensive exploration has been done on those two continents and deposits are correspondingly less likely to remain undiscovered.

PROSPECTING TECHNIQUES

Sophisticated technical methods for prospecting barite deposits have not yet been developed, chiefly because new deposits have been fairly easy to find in known districts. The success of future prospecting will be increased if prospecting is guided by a knowledge of geologic associations and the role of barite in the sedimentary environment. Deposits should be sought in residuum overlying carbonate-rich rocks, especially those of Cambrian or Ordovician age. Other areas of well-weathered rocks that have been hosts for veins or pods of barite also should be examined. The fetid black beds of barite occur abundantly in sequences of dark siliceous rocks of mid-Paleozoic age. The widespread, but probably mistaken, idea that the black bedded deposits must be of hydrothermal origin has diverted the attention of prospectors from search in sedimentary basins that lack intrusive igneous rocks. Geochemical techniques may be helpful in prospecting for barite deposits because increased concentration of barium has been noticed in rocks enclosing barite-rich zones in Arkansas (Brobst and Ward, 1965). Gravimetric surveys have potential use in prospecting (Uhley and Scharon, 1954).

PROBLEMS FOR RESEARCH

Research on problems relating to the evaluation of barite resources has one focal point: to get the information necessary to convert hypothetical and speculative resources to identified resources, which is a fundamental reason for doing research on the geology of any mineral commodity.

Further studies of the geochemistry of barium are needed to understand the processes at work in the mobilization, transportation, and concentration of barium, especially in the sedimentary environment. The role of connate water in the formation of barite deposits requires further examination. Barium is an abundant accessory element in the ash of many coals and in some Alaskan oil shales; this fact suggests that factors leading to the concentration of the organic materials favor the concentration of barium. The function of organic materials and bacterial processes in precipitating barium is a virtually unexplored field and should be investigated. A question remains about the so-called residual barite deposits: Does the barite of these deposits become concentrated mechanically or are solution and redeposition of the barite also involved? The relation of bedded barite deposits to bedded phosphate deposits needs examination. New information about any of these subjects should help to define new areas and targets worthy of exploration for barite.

The close association of barium minerals with those of fluorine, rare earths, manganese, lead, zinc, and precious metals in vein deposits should be studied further. The use of barium as a tracer in the search for deposits of other coexisting elements

has not been tested thoroughly.

Better conservation of barium would be possible if supplies of barite available as a coproduct were utilized more fully. Techniques also might be developed to extend known barite resources through the reuse of barite and barium products, almost none of which are recovered for reuse in today's salvage and recycling operations.

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BERYLLIUM

By Wallace R. Griffitts

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ABSTRACT OF CONCLUSIONS

Beryllium metal is used in a variety of products in which its low density and other physical properties are particularly valuable. More than half the metal produced is used with copper in strong, fatigue-resistant alloys. Beryllium oxide and beryl are used in many ceramic and other products. The total amount used is small; less than 1,000 tons of beryllium was used in all forms in the year of highest consumption. The annual consumption may increase to as much as 4,000 tons by the year 2000.

About 95 percent of the beryllium ore used in the United States has been imported, three-fourths of it coming from Brazil, the Republic of South Africa, India, Argentina, and Mozambique. Significant domestic production began in 1969 and probably will increase until it accounts for at least half the ore consumed.

The resources of beryllium in known domestic deposits are estimated at 60,000 tons, and these can be increased by further exploration to become sufficient to supply our needs for many decades.

INTRODUCTION

The beryllium industry is both small and young as compared with most base-, ferrous-, and light-metal industries. Beryllium thus is one of many minor commodities, one that has been rather highly publicized because of glamorous actual and potential uses in nuclear energy and manufacture of space vehicles. Nonetheless, many important uses for beryllium have developed during the 40 years since production began. The industry is shifting from complete dependence upon imported beryl concentrates derived from small pegmatitic deposits to the mining of large domestic nonpegmatitic deposits. Deposits containing 60,000 tons of metal—enough to satisfy national needs for several decades—were found in about 10 years. More deposits doubtless can be found if markets develop sufficiently to stimulate prospecting.

PROPERTIES AND USES OF THE METAL

Beryllium, with a specific gravity of 1.85, is one of the lightest metals stable in air. Like aluminum,

it develops a coherent oxide coating when exposed to air, which protects it from further oxidation and increases its apparent hardness. Unfortunately, oxygen-free beryllium metal is very difficult to prepare. Most metal in commerce contains nearly 2 percent oxygen, which contributes to its brittleness. This brittleness requires production of articles by powder metallurgy and machining—a costly procedure—and limits reshaping by rolling or drawing.

The high thermal conductivity, high melting point, high specific heat, low density, and rigidity of the metal make it useful in heat sinks and in specialized structural elements for aircraft and spacecraft. Its low neutron absorption and its emission of neutrons under appropriate gamma or alpha bombardment lead to uses in nuclear energy. In the early 1970's, nearly 20 percent of the beryllium extracted was used as the metal.

PROPERTIES AND USES OF BERYLLIUM ALLOYS

More than half the beryllium reduced from its ore is used in alloys, principally in beryllium-copper alloys containing about 2 percent beryllium and about 0.2 percent nickel or cobalt. These alloys have the greatest strength and wear resistance of any nonmagnetic material, with a tensile strength about twice that of hard-drawn iron and two-thirds that of mild steel. They also are excellent conductors of electricity and heat and are very resistant to corrosion. Below a temperature of about 300°F, they are much more resistant to fatigue than steel. They are much used in springs, electrical connectors, and many other specialized items. The use of the alloys in computers and other electrical equipment has resulted in greatly increased consumption during the last 20 years.

Beryllium has been used in small amounts with nickel to make hardenable alloys with very high tensile strength that are usable at higher temperatures than copper alloys.

In light alloys with aluminum and magnesium, beryllium can improve the properties or facilitate the production of the metal. Addition of 0.02 percent of beryllium to aluminum-magnesium alloys reduces reaction with green sand molds and improves oxidation resistance. It eliminates the need for elaborate precautions against burning of magnesium, inasmuch as the molten metal containing beryllium can be poured safely at a temperature of 1,400°F. "Lockalloy," containing 62 percent beryllium and 38 percent aluminum, has some of the desirable properties of beryllium, is reasonably workable, and can be used at temperatures as high as 800°F. Various composite materials containing beryllium in nonbrittle matrices are strong and light.

PROPERTIES AND USES OF THE OXIDE

Beryllium oxide is the third major form in which beryllium is used. This oxide, with a high melting point, a high thermal conductivity, and very low electrical conductivity, can be used as an electrical insulator in applications where heat must be transferred or dissipated, as in power transistors. The high thermal conductivity results in high thermal shock resistance, which is important in special ceramics. These, and the nuclear properties, lead to the use of beryllium oxide in reactor fuel elements.

BERYL AS AN INDUSTRIAL MINERAL

In addition to the uses of beryllium that require extraction of the metal from its ore, there are many uses that are met by incorporating undecomposed beryl into an industrial product. These uses account for about one-tenth of the beryl ore used during the last 20 years. Some of these uses are chemical—the addition of beryllium to a ceramic or glass mix; others rely upon one or more physical properties of the mineral beryl itself such as its structure, its thermal conductivity, or its ability to adhere to plastics.

END USES OF BERYLLIUM

The amount of beryllium used in various ways in the United States is summarized in table 15.

TABLE 15.—*End uses of beryllium in the United States, 1968*

[Data from Heindl, 1970, p. 498]

Use	Short tons	Percent of total
Nuclear applications	35	10
Guided missiles and space vehicles	35	10
Instruments	45	13
Switch gear	90	26
Welding equipment	40	11
Electronic computers	40	11
Radio and television equipment	25	6
Other	38	13
Total	348	100

SECONDARY RECOVERY

Much recoverable beryllium scrap is produced in making articles out of beryllium metal. This is an inevitable result of the necessity of making blank or roughly formed pieces of metal by powder metallurgy, then machining the final product from them. Not much metal, however, can be salvaged from the final articles. Components of missiles and rockets are commonly destroyed in use, whereas those of manned capsules and orbiting observatories may be

recoverable. Many beryllium aircraft parts can readily be salvaged; so can beryllium used in nuclear energy establishments, if it is not too strongly contaminated by radioactive substances. Beryllium-copper alloy is used mostly to make very small items and this beryllium generally cannot be salvaged. The same is to a large extent true of the beryllium in ceramic ware, whether high or low in BeO.

TOXICITY OF BERYLLIUM AND ITS COMPOUNDS

Much was written during the 1940's and 1950's about the toxicity of beryllium and its compounds. Subsequent studies have shown that the ores are not hazardous and that industrial products can be handled safely with reasonable precautions. The toxicity has caused few restrictions on its use, the most notable being its elimination from phosphors in fluorescent lamps and its exclusion from the fuel of most rockets.

HISTORY OF PRODUCTION AND CONSUMPTION

The beryllium industry is rather new; commercial production began in the United States in 1932. Consumption increased steadily until 1943, as indicated in figure 11. After the World War II stimulus and the postwar slump, ore consumption increased rather steadily until about 1960, but since then it has not changed greatly. In most years imports of beryl ore have exceeded consumption, and stockpiles have accumulated. The opening of the beryllium mine near Delta, Utah, in 1969, and release of ore from the Federal stockpile are at least partly responsible for the relatively low imports in 1970 and 1971. This proportion of imports probably will continue, with about half of the U.S. needs imported, the other half produced domestically. Thus, increasing amounts of beryllium will be obtained from

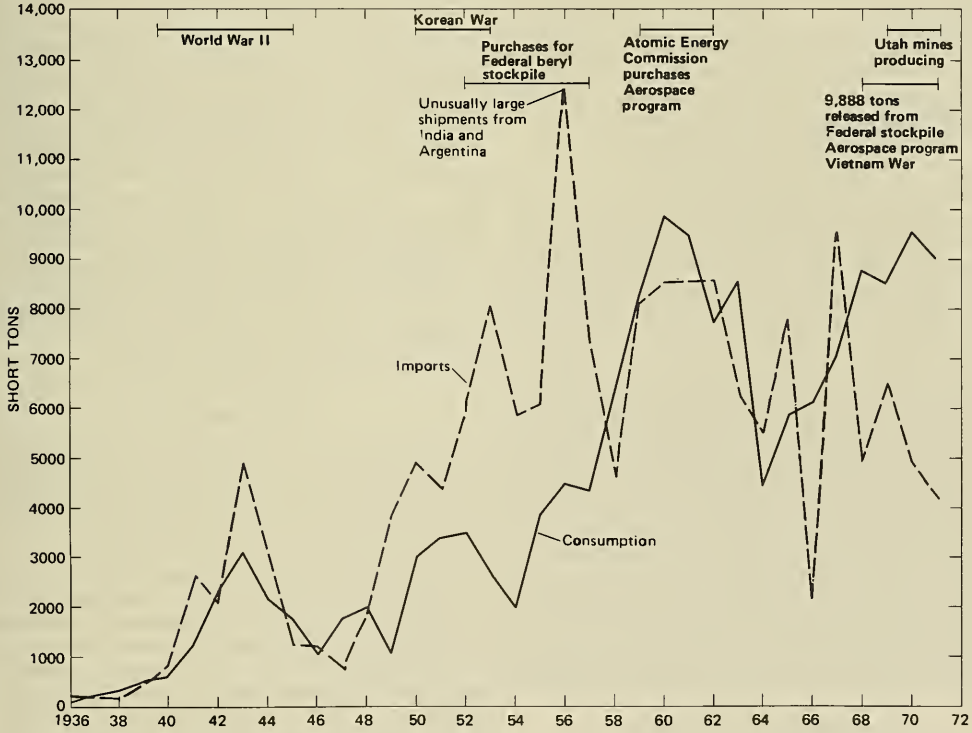

FIGURE 11.—Beryl ore imported and consumed by U.S. industry, 1936–71. Nonberyl ore, recalculated to equivalent amounts of beryl ore, not important before 1969. Data from U.S. Bureau of Mines Minerals Yearbooks.

nonberyl ores. Nonberyl ores were recalculated as equivalent amounts of beryl in preparing figure 11. There has otherwise been little change in the sources (table 16) since 1939, when Brazil first became a major exporter. One evident feature is the decreasing portion mined within the United States.

TABLE 16.—*Sources of beryl ore used in the industry of the United States*

[Data from U.S. Bureau of Mines, 1953; 1953–69]

Country	Percent of total		
	1936–51	1952–59	1960–68
Brazil	49	27	32
Republic of South Africa	10	11	5
India	8	11	13
Argentina	12	15	10
Mozambique	2	13	10
United States	10	5	4
Zaire	-----	5	7
Rhodesia	4	7	3
Kenya and Uganda	-----	<1	8
Australia	4	2	5
Malagasy Republic	-----	2	3
Portugal	-----	2	<1
Other	1	<1	<1
Total tons beryl (rounded)	32,000	98,000	161,000

FUTURE CONSUMPTION

The history of beryllium use has been one of diversification. The metal has gone into many end products, no one of which has been a very large part of the total. The rate of growth, therefore, has been rather steady for many years, following an exponential curve; the major fluctuations result from sporadic government programs in armaments, nuclear energy, and space. The assured supply of raw material from Spor Mountain, Utah, doubtless will encourage the development of additional uses by potential consumers who lack confidence in a dependable supply of imported beryl ore. It is likely, even, that this new source of ore will stimulate uses sufficiently to bolster the market for beryl. Consumption may well increase threefold or fourfold by the year 2000, with the use in that year of 3,000–4,000 tons of beryllium in all forms. About 4,500 tons of metal would then have been used of our total known domestic resources of about 60,000 tons. Perhaps the use in light alloys—with aluminum and magnesium—will increase more than other uses.

EXTRACTIVE METHODS

To extract beryllium, beryl ore is heated, with or without fluxes, and then is leached to give an aqueous solution of beryllium fluoride or sulfate. In the United States, Kawecki-Berylco Industries sinter finely pulverized beryl with fluorides and sodium carbonate, then leach the sintered material with water to obtain a beryllium-fluoride solution from which beryllium hydroxide is precipitated. Brush-Wellman Co., in an alternate process, fuses lump beryl ore, quenches the melt, and leaches the beryllium with sulfuric acid. Ore can also be mixed with a carbonate flux, fused, then leached with sulfuric acid. The nonberyl ore from Spor Mountain, Utah, yields its beryllium upon leaching with sulfuric acid with no pretreatment. All these procedures can extract more than 90 percent of the beryllium in the ore.

The different extraction methods are not equally applicable to all types of ore, and therefore are of significance in assessing the resource potential of various beryllium-rich materials. The fuse-quench method is well adapted to coarse beryl ore, but not to low-grade ore, nonberyl ore, or to fine-grained concentrates. The fluoride-sintering method requires fine grinding of ore and can readily handle flotation concentrates, even if the beryllium is contained in minerals other than beryl. Apatite and fluorite, which commonly accompany beryl in pegmatitic and hydrothermal deposits, respectively, reduce the extractability of beryllium by the fluoride method but not by carbonate fusion–sulfuric acid leach methods; these methods may therefore come into use despite their comparatively high reagent costs.

The novel extractive procedure developed for use with the ores of Spor Mountain, Utah, may be the precursor of markedly modified or new technologies for use on other nonpegmatitic ores.

GEOLOGIC ENVIRONMENT

GEOCHEMISTRY

Beryllium has one stable isotope, Be^9, which is the only one involved in industrial use and in most geochemical and geological processes. Three unstable isotopes, Be^7, Be^8, and Be^{10}, are produced by cosmic-ray interaction with the upper atmosphere.

The beryllium content of the earth's crust is estimated to be 2–3.5 ppm (parts per million). All but a very small percentage of this metal is contained in the common rock-forming minerals and not in beryllium-rich minerals. This dispersal is caused by its ability to replace silicon—its ionic radius (0.31 A) is near that of the silicon ion (0.41 A). However, because of the difference in charge (+2 instead of +4), the difference in size, and the greater tendency of beryllium to form covalent bonds, the

substitution of beryllium for silicon impairs the stability of a crystal's structure. Hence, beryllium is most concentrated in minerals whose structures are most tolerant of the resulting distortion. Plagioclase feldspar probably contains much of the earth's beryllium, but micas and clays are also important hosts.

During the crystallization of a magma, beryllium becomes progressively more concentrated in the fluid as crystallization proceeds. One result of this is an increasing concentration of beryllium in successively younger rocks in genetically related suites. This enrichment reaches a point where beryllium minerals can form only in the presence of complexing agents, such as F^- or CO_3^{-2}, that keep an unusually large proportion of the beryllium in the residual liquids. In igneous rocks the beryllium content therefore increases along with silica and alkali contents. The average content of beryllium in peridotite is less than 0.25 ppm, that of basalt and gabbro is about 0.5 ppm, and that of rhyolite and granite is about 5 ppm. Detailed study of each of these groups shows the relations to be complex. For example, in silicic rocks the beryllium content passes through a maximum as silica content increases. In addition, the average beryllium content of plutonic rocks is higher than that of volcanic rocks, perhaps reflecting the loss of beryllium in vapors during volcanism.

The very coarse texture of pegmatites has made them difficult to sample for beryllium content, although the coarseness facilitates the determination in the field of the contents of beryl and other economic minerals.

In a series of related pegmatites, the beryllium content can increase in successively intruded rocks to a maximum of about 180 ppm; it then remains rather uniform. This is apparently the maximum concentration that can be reached through magmatic processes in magmas of granitic composition. Much higher beryllium contents may characterize beryl-rich inner zones of pegmatite dikes, but averaging these with the larger beryl-poor outer zones shows that few, if any, bodies contain more than 200 ppm overall, which corresponds to about one-half of 1 percent beryl. This is the maximum grade that can be expected in large bodies of pegmatite. Most pegmatites contain much less and may average a few tons of parts per million of beryllium.

Beryllium is very scarce in most hydrothermal deposits, generally constituting 1 ppm or less. Ores formed by replacement commonly contain about as much beryllium as the rock that was replaced. For example, most tactites in limestone contain less than 1 ppm beryllium, and replacement veins in granite or gneiss commonly contain a few parts per million. Certain hydrothermal deposits are low in base and precious metals but are rich in beryllium. They generally contain fluorite, magnetite or hematite, carbonate minerals, zinc minerals, and if fluoritic, one or more metals that, like beryllium, form water-soluble fluoride complexes, such as tin, tungsten, bismuth, manganese, rare earths, titanium, or niobium. These metals are largely in oxygen compounds; sulfide minerals are rather uncommon.

Beryllium is released from the rock-forming minerals as they weather, and is incorporated in clay minerals. Thereafter, it remains in clayey soil or is carried off in suspension in running water. Most coarse sedimentary materials—pebbles, sand, and derived rocks—have low beryllium contents, corresponding to that of the quartz that is generally the dominant component. Near beryllium deposits, coarse sediments may contain detrital particles of beryllium minerals, many of which are resistant to weathering. Industrial beryl, and gem chrysoberyl, phenakite, and euclase ($AlBeSiO_4(OH)$) have been mined from such extremely local concentrations. Very little migration of beryllium takes place in solution in normal waters because the beryllium released upon weathering is quickly adsorbed by mineral particles. High acid or carbonate- or halide-rich water can cause small-scale migration of beryllium, but not on an economically important scale.

The beryllium contents of rocks change very little with metamorphism. Thus, most micaceous metamorphic rocks contain a few parts per million of beryllium, and quartzite and marble contain very little.

MINERALS

The only beryllium mineral that has had much economic importance is beryl, which has yielded nearly all the beryllium used in industry. Bertrandite, phenakite, helvite, chrysoberyl, and barylite are known to occur in moderately large deposits. The other 39 known beryllium minerals have been found in only small amounts. It is possible that some of them will become important, as bertrandite and barylite have. Twenty years ago bertrandite and barylite were thought to be very rare, but now they are known to form large bodies of present or potential economic value. The common or important minerals are shown in table 17.

TYPES OF BERYLLIUM DEPOSITS

Beryllium deposits can be divided into two broad categories: (1) pegmatitic, and (2) nonpegmatitic

TABLE 17.—*Characteristics of berryllium minerals known to form large deposits*

Mineral	Usual BeO content (percent)	Hardness	Specific gravity	Common colors	Size of grains	Associated minerals	
						Pegmatitic deposits	Nonpegmatitic deposits
Beryl ($Be_3Al_2Si_6O_{18}$)	12–13.5	7.5	2.6 –2.9	White, pale blue, or green.	<0.1 inch–2 feet	Quartz, sodic plagioclase, microcline, muscovite, spodumene.	Quartz, fluorite, carbonates, iron oxide minerals.
Bertrandite ($Be_4Si_2O_7(OH)_2$).	42	6	2.6	White	<0.001–⅛ inch.	Beryl, quartz, feldspars.	Quartz, beryl, fluorites, carbonates, iron oxide minerals.
Phenakite (Be_2SiO_4)	45	7.5	2.9 –3.0	White	<0.1–2 inches.	Beryl, quartz, feldspars, fluorite, topaz.	Beryl, fluorite, topaz carbonates.
Chrysoberyl (Al_2BeO_4)	19.8	8.5	3.5 –3.8	Green, yellow.	<0.1–2 inches.	Microcline, sodic plagioclase, quartz, beryl, mica.	Fluorite, disapore, tourmaline.
Helvite ($(Mn,Fe,Zn_4)Be_3Si_3O_{12}S$).	11–14	5.5–6.5	3.16–3.66	Brown, yellow, gray.	<0.1–3 inches.	Feldspars, quartz, fluorite.	Quartz, fluorite, carbonates, iron oxide minerals.
Barylite ($BaBe_2Si_2O_7$)	16	7	4	White, yellow.	<0.1 inch.	----------	Quartz, albite, carbonates, sodic amphiboles.

or hydrothermal. Each of these must be further subdivided: the pegmatitic into fine-grained unzoned deposits and coarse-grained zoned deposits; the hydrothermal deposits into several categories, in general conforming to Lindgren's classification of hypothermal, mesothermal, and epithermal.

PEGMATITIC DEPOSITS

The pegmatitic deposits that are significant as sources of beryllium minerals are composed of major amounts of quartz, sodic plagioclase, and microcline, with or without spodumene, muscovite, or lepidolite. The association of beryl with spodumene is close, and few spodumene-bearing pegmatites lack beryl. Muscovite is also a common associate of beryl, especially in nonlithian pegmatites. Commonly, however, the muscovite found with beryl will not yield sheet mica, which limits the production of beryl as a byproduct from mica mines.

The fine-grained unzoned pegmatite dikes that have attracted most attention as potential sources of beryl are aggregates of albite, microcline, spodumene, quartz, beryl, and muscovite. These are moderately uniform in composition, differing from place to place mainly in the size and orientation of the mineral particles. Spodumene and microcline crystals range in maximum dimension from a fraction of an inch to a few feet, and lathlike crystals of spodumene may be parallel or random in orientation. Albite, quartz, muscovite, and beryl form a fine-grained matrix that surrounds the spodumene, microcline, and lumps of quartz. Fine-grained beryl, generally white, constitutes about ½ percent of the pegmatite.

These pegmatites are important sources of spodumene, scrap mica, and feldspar, but the small amount and fine grain size of the beryl have prevented its recovery, even in conjunction with flotation of the other minerals.

Most zoned pegmatites are composed of the same minerals as the unzoned pegmatites. They differ in that the proportions of minerals and the textures of the rocks vary markedly from place to place in a dike, generally changing from the wall to the core of the pegmatite body. This internal structure of pegmatite dikes is uniform throughout the world. Near the walls the rock consists of plagioclase and quartz, with or without muscovite or microcline, and it has a very coarse granitic texture. Toward the center of the dike, this composition gives way to a zone of blocky microcline that may be monomineralic or may contain plagioclase and quartz interstitial to the microcline blocks. The center of the dike is occupied by a core of quartz. The margins of the quartz core are the loci of crystals of beryl; some crystals are very large, 3 feet or more wide and 20 feet long. The beryl is not evenly distributed along the margins of the cores but is in pockets separated by barren rock.

The much less common, but more spectacular, zoned lithian pegmatites usually have spodumene-bearing zones between the microcline-rich zone and the quartz core. Many of these zones are rather similar in composition to the unzoned spodumene-

bearing pegmatites. The crystals of spodumene and beryl may be very large, which permits them to be recovered by hand sorting in rather simple mining operations.

The coarse zoned pegmatites have yielded nearly all the beryl used in industry.

HYDROTHERMAL DEPOSITS

The hydrothermal deposits that are of most interest as actual or potential sources of beryllium ore are mainly hypothermal types formed at high temperature and at least moderate depth, and epithermal types formed at shallow depths. These deposits have provided a very small proportion of the total supply of ore but will become dominant in the near future.

HYPOTHERMAL DEPOSITS

Hypothermal deposits are generally quartz-rich moderately coarse-grained veins and beryl-bearing granite, both associated with greisen. In North America they are most commonly mined for tungsten, but a few have yielded tin minerals, and the ones near Lake George, Colo., were mined for beryl and bertrandite. Other examples of beryllium-bearing hypothermal deposits are those near Lost River, Alaska; in the Bagdad area, Arizona; in the Mineral and Sheeprock Ranges, Utah; and in the Mount Wheeler and Eureka areas, Nevada. Most of these are veins in silicate rocks; a few, as in Nevada, are in carbonate rocks; and in the Sheeprock and Mineral Ranges beryl is dispersed in granite.

Contact-metasomatic deposits are hypothermal replacement bodies in carbonate rocks, most commonly along or near contacts of intrusive rocks. They contain a wide variety of silicate minerals and, rather uncommonly, helvite. Much of the beryllium reported in these deposits is contained in idocrase or other minerals of low-beryllium content. The deposits at Iron Mountain, N. Mex., have been thoroughly studied. Others are at Iron Mountain, N.H., and in the Victorio Mountains, N. Mex.

MESOTHERMAL DEPOSITS

The mesothermal deposits that yield most of our lead, zinc, and copper are notably poor in beryllium. A little helvite has been found in deposits rich in rhodochrosite or rhodonite near Philipsburg, Mont., and Silverton, Colo., but these deposits show no promise as sources of beryllium.

For convenience, the chrysoberyl deposits of the Seward Peninsula, Alaska, are included here, although they might also be grouped with the hypothermal deposits with which they are associated. These replacement bodies in limestone consist largely of very fine grained fluorite, diaspore, and chrysoberyl, and they lack silicate gangue minerals. They contain some of the largest known resources of beryllium and of fluorite and may form the basis for a multiproduct mining operation.

EPITHERMAL DEPOSITS

Concentrations of beryllium minerals in epithermal deposits were overlooked for many years because they are not closely associated with the famous gold- and silver-bearing sulfide deposits of this genetic type. Instead, they are in sulfide-poor altered rocks that contain small amounts of fluorite as the only readily recognizable economic mineral. The largest known beryllium deposits are the epithermal mantos at Spor Mountain, Utah, in which a rhyolite ash bed containing as much as 65 percent of limestone and dolomite in pebbles and cobbles was replaced by montmorillonite, silica, fluorite, adularia, and bertrandite. The ore is too fine grained to be beneficiated, but nearly all the beryllium can be leached from it with acid. A somewhat similar deposit is a few miles north of Iron Mountain, N. Mex.

Large veins of quartz, calcite, adularia, and bertrandite cut monzonite in the Gold Hill district, Utah, and are unusual in that they contain no fluorite and are not in calcareous host rocks.

REGIONAL DISTRIBUTION OF BERYLLIUM DEPOSITS

Pegmatite deposits of Paleozoic age have been found along much of the Appalachian Mountains from Nova Scotia to central Alabama. Beryl is widespread in the northern Appalachians, but is largely restricted in the southern Appalachians to the tin-spodumene belt near Kings Mountain, N.C., the Amelia-Powhatan County area, Virginia, and the Troup County area, Georgia. Pegmatites of Precambrian age yield beryl in the Black Hills, S. Dak., northern Colorado, northern New Mexico, and south-central Wyoming. Beryl-bearing pegmatites are not as productive elsewhere in the west.

Nonpegmatitic deposits have an entirely different distribution. Most are in the block-faulted regions of the West, and a few are in strongly faulted areas in Alaska, the Mississippi Valley, and northern New England. The beryllium deposits are in, and probably are features of, fluorspar metallogenic provinces, especially in the West, where they commonly are associated with igneous rocks of middle or late Tertiary age. Many of the deposits are in limestone or dolomite.

RESOURCES

The only resources that have been reasonably well delineated in pegmatites are those in the fine-grained spodumene-bearing pegmatites that are being mined for lithium. These contain a very large amount of beryl; 800,000 tons has been estimated to be in the pegmatites of North and South Carolina alone. However, because of the low beryl content of the rock (about one-half of 1 percent) and its fine particle size, this beryl will not be economically recoverable. Hence, it is not included in the resource tabulation.

The coarse zoned pegmatites, on the other hand, contain beryl that is readily recoverable, but the known beryl resources are no more than 10,000 tons, because no exploration is done in advance of mining.

The larger nonpegmatitic deposits are persistent enough to be explored thoroughly before mining and to yield fairly reliable resource estimates with minimal exploration. The three largest districts, Spor Mountain, Utah; Seward Peninsula, Alaska; and Gold Hill, Utah, account for most of the resources of beryllium in known nonpegmatitic deposits as given in table 18.

TABLE 18.—*Estimated resources of beryllium, in short tons of metal*

	In known deposits		In undiscovered deposits	
	Pegmatitic	Nonpegmatitic	Pegmatitic	Nonpegmatitic
United States	300	60,000	600	250,000
Other countries	600	32,000	4,500	400,000

The 60,000 tons of beryllium in nonpegmatitic deposits in the United States are in deposits discovered in a period of about 10 years, after which exploration abruptly ceased. Additional deposits doubtless remain to be discovered. These are assumed to contain about four times as much beryllium as the deposits that are now known. The following characteristics of major districts were used in evaluating potential future discoveries: most beryllium districts (1) are associated with high-angle faults of regional extent, generally block faults; (2) are in fluorite metallogenic provinces; and (3) have calcareous rocks as the most favorable host for mineralization. Figure 12 shows areas that are most promising for additional exploration. It

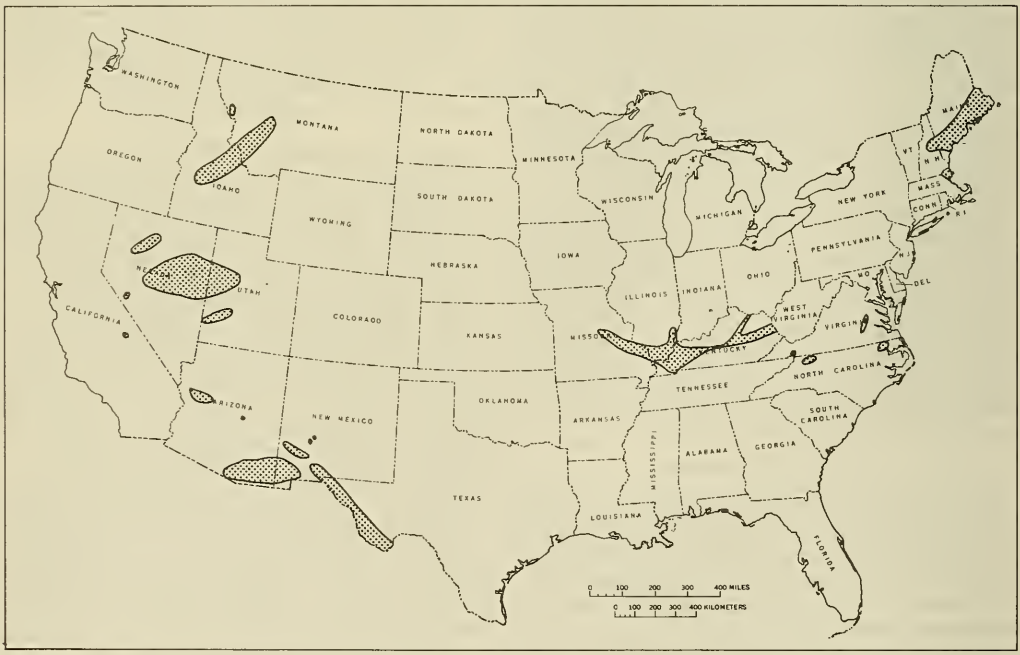

FIGURE 12.—Areas of the conterminous United States in which beryllium deposits are most likely to be found.

should be emphasized that the diagnostic characteristics given above pertain to most, but not all districts. Beryllium districts may well be found that do not conform to these generalizations, but their potential cannot now be estimated.

Beryllium minerals of hydrothermal deposits seldom can be recognized readily in the field, and the deposits themselves are likely to be covered by soil. Hence, they are most likely to be found by a study of regional geology, followed by geochemical surveys of the most promising areas. Resources now known are large, but small-scale search is justified for deposits that might be better economically than those that are now known.

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BISMUTH

By J. W. Hasler, M. H. Miller, and R. M. Chapman

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ABSTRACT OF CONCLUSIONS

In the United States, bismuth is largely a byproduct from ores of other metals with which it is associated, principally lead and copper. Lesser amounts of bismuth are found in molybdenum, gold, silver, tin, tungsten, and zinc ores. The United States consumes annually as much as four times the amount of bismuth recovered from domestic ores; thus, the United States must rely on imports for 50–75 percent of its supply. The three principal uses of bismuth in the United States at present are in the manufacture of pharmaceuticals (medicines and pearlescent cosmetics), low-melting alloys, and metallurgical additives.

A continued supply of bismuth must come as a byproduct from the major producers of lead, zinc, and copper in the Western United States. Other potential sources in the United States are molybdenum and tungsten ores, coal ash from West Virginia coals, and oceanic manganese nodules. Bismuth is known to occur in lead deposits in the Appalachian Mountains from North Carolina to Maine. Host rocks include Precambrian dolomites west of the Adirondack Mountains in New York and Precambrian and Cambrian schists east of the Blue Ridge in North Carolina. Bismuth content of some metamorphic rocks in the Piedmont province is relatively high. Pegmatites in southeastern Pennsylvania and in western Maine commonly carry native bismuth and bismuthinite in small amounts.

Should lead production be curtailed by continued closings of smelters, especially those with bismuth recovery units, the domestic supply of bismuth will be seriously affected; consequently, research and exploration for bismuth-bearing minerals should be continued.

INTRODUCTION

Bismuth is obtained largely as a byproduct from ores of other metals, principally lead and copper. Lesser amounts of bismuth are associated with molybdenum, cobalt, gold, silver, tin, tungsten, and zinc. Despite its quantitative scarcity, the frequency of occurrence of bismuth is remarkably high. The bismuth minerals bismite (Bi_2O_3) and bismuthinite (Bi_2S_3) are widely distributed in small quantities in ores throughout all the continents (Paone, 1970). Bismuth reserves in the United States are dependent on western U.S. lead reserves, which average about 7 pounds bismuth per ton of lead (0.35 percent), or 100 ppm (parts per million) bismuth in 3-percent lead ore (R. L. Erickson, written commun., 1972).

Free-world countries known to have major bismuth reserves are Japan, 95,200,000 pounds; Mexico, 25 million pounds; and Peru, 20 million pounds. Bolivia, Canada, South Korea, France, and Yugoslavia together have a reserve of about 18 million pounds (U.S. Department of the Interior, 1972, p. 24–26).

The principal uses for bismuth are in low-melting alloys, in metallurgical additives for aluminum, carbon steel, and malleable iron, in pearlescent cosmetic pigments, in medicines, and in a variety of other smaller specialized applications. The largest single use of bismuth continues to be in the pharmaceutical field.

Small quantities of bismuth compounds are used as an accelerating agent in the rubber vulcanizing process. A bismuth-cadmium alloy is used in the production of some selenium rectifiers, and a few thousand pounds of metal is consumed each year in the manufacture of bismuth-tellurium electronic

devices. Experimental uses and some laboratory reagent chemicals account for small additional quantities (Bancel, 1971).

The future for bismuth seems good. However, much of the demand for bismuth depends somewhat on the state of health of the aircraft and automobile industries. These affect lead production, and increased lead production should normally increase bismuth production.

The search for new and undiscovered sources of bismuth will correspond to the search for bismuth's associated metals, such as cobalt, copper, gold, lead, molybdenum, silver, tin, tungsten, and zinc. Ash from some coals contains as much as 0.003 percent bismuth, or 30 ppm (Goldschmidt, 1935).

Estimated annual production of bismuth in the United States ranged from 590,000 pounds in 1962 to approximately 850,000 pounds in 1971. These figures probably include some bismuth produced in the United States from foreign ores. The United States consumed from 2,175,038 to 3,199,321 pounds of bismuth metal annually during 1963–70; in 1971, consumption dropped to 1,648,718 pounds. World bismuth production in 1971 (excluding People's Republic of China and U.S.S.R.) totaled 7,990,000 pounds (Cook, 1972).

U.S. bismuth demand is forecast to increase at an annual rate of 3 percent, and the domestic consumption in the year 2000 is estimated to range from 3 to 5.2 million pounds (Charlie Wyche, oral commun., 1972). Though the supply of bismuth seems assured, exploration cutbacks, production problems (such as strikes, continued smelter closings, or mine fires), or nationalization of foreign mines may result in a reduction of much-needed imports as well as domestic production. The bismuth supply situation could then become most critical.

EXPLOITATION

Bismuth, a metallic element, was probably unknown to the Greeks and Romans; in the Middle Ages it became familiar but was frequently confused with other metals, such as tin, lead, antimony, and zinc. In the 15th century Basil Valentine referred to it as "wismit." About 1597, the efficacy of bismuth nitrate in treating intestinal disorders was discovered by Andreas Lebanius, and the element has been used for that purpose to the present. However, it was not until the 18th century that J. H. Pott, C. J. Geoffrey, and T. Bergman produced pure bismuth metal. Beginning in 1833 with the Pattison process for desilverization of lead bullion and attendant extraction of bismuth alloy, continued development and improvement of metallurgical processes for extraction and purification of bismuth have resulted in commercial availability of bismuth metal of 97.995 percent purity.

Bismuth compounds were noted initially for their soothing effects on human digestive disorders and healing effects on wounds and sores. This property of bismuth was exploited in many medicinal and cosmetic preparations, and until 1930 some 90 percent of the bismuth used was for this purpose. The development of low-melting alloys has since resulted in a wide variety of industrial applications of bismuth alloys and chemical compounds such as metallurgical additives for aluminum, carbon steel, and malleable iron and in pearlescent pigments. The major current uses for metallic bismuth depend on its ability to impart fusibility and machinability to a variety of alloys. The United States consumes considerably more bismuth than is recovered from domestic ores and must therefore rely on imports for 50–75 percent of its supply (Persse, 1970). Major sources of imports in 1971 were Mexico, Japan, and Peru. Refinery production of bismuth in the United States is mainly from the American Smelting and Refining Co. in Omaha, Nebr.; U.S. Smelting, Refining, and Mining Co. at East Chicago, Ind.; and Southern California Chemical Co., Los Nietos, Calif.

Reductions in lead production and subsequent closures of any lead refining facilities will seriously affect the bismuth supply in the United States. Current environmental problems are having a serious impact on the domestic mining industry and will continue until such problems can be solved.

GEOLOGIC ENVIRONMENT

GEOCHEMISTRY

The average bismuth content of the earth's crust is estimated at 0.1 ppm or one part in 10 million. Bismuth's abundance is reported to be highest in oceanic manganese nodules, where it ranges from 0.5 to 24 ppm, and is next highest in silicic rocks, in which it ranges from 0.02 to 0.9 ppm (Michael Fleischer, written commun., 1970). Analyses from various sources indicate that the abundance of bismuth in coal ash may be as much as 0.003 percent, or 30 ppm (Goldschmidt, 1935).

Bismuth, like arsenic and antimony, is chalcophile, and all three show a strong affinity for sulfur. Most bismuth-bearing minerals crystallize in late magmatic stages or are deposited by relatively hot hydrothermal solutions. Throughout the geochemical cycle, bismuth is comparatively readily precipitated as basic carbonate which forms during the hydrolytic decomposition of bismuth salts in aqueous solution.

Bismuth, therefore, becomes concentrated in the hydrolyzates. Although the biological role is unknown, bismuth is known to occur in some marine organisms (Rankama and Sahama, 1950).

BISMUTH ORES

Most bismuth produced in the United States is a byproduct of lead refineries which treat crude bullion, flue dust, and other metallurgical products. The bismuth content of ores and concentrates is generally so low that it is not reported in assays, even from mines known to be relatively rich in bismuth; thus the primary sources of bismuth are known only in a general way (Cooper, 1962).

MAJOR SOURCES

Hypogene deposits in the Western United States account for most of the domestic bismuth production. These deposits generally formed at high to medium temperatures, commonly within or near intrusive igneous rocks. A few small pockets of bismuth ore have been mined from pegmatite dikes, quartz veins, and contact-metamorphic deposits, but most of the bismuth occurs as a minor constituent of ores of silver, lead, zinc, copper, gold, tungsten, and molybdenum. Lead and lead-zinc ores that are high in bismuth also tend to be high in silver, gold, and commonly copper. A distinct association of bismuth with silver is apparent in some mines.

Lead-zinc-silver replacement deposits in limestone have probably been the most important sources of bismuth in the United States. Deposits of this type occur at Leadville and Gilman, Colo.; Tintic and Little Cottonwood, Utah; Darwin, Calif.; and Patagonia, Ariz. In these deposits the bismuth occurs in the oxidized as well as in the sulfide ores. Primary bismuth minerals, where known, include bismuth sulfosalts of lead, silver, and copper, bismuthinite, and native bismuth.

Complex lead-copper-silver-bismuth ores have been mined in the Red Mountain, Poughkeepsie Gulch, Upper Uncompahgre, Mineral Point, Engineer Mountain, and Lake City districts in the San Juan Mountains, Colo., and also in the Montezuma district in the Front Range, Colo. The ore bodies are small, but some are very rich in bismuth and precious metals.

In the Coeur d'Alene district, Idaho, bismuth in recoverable amounts has been reported from the Sunshine mine and certain other mines in the "Silver Belt." Gold-bismuth ores are reported from gold deposits in Riverside County, Calif., and Grant County, N. Mex. Relatively abundant bismuth minerals are reported in complex gold ores of the Boise Basin district, Idaho; the Goldfield and Yellow Pine districts, Nevada; and the Argenta and Elkhorn districts, Montana. Lead and zinc ores and concentrates from deposits of the Mississippi Valley type contain no detectable bismuth.

MINOR OCCURRENCES

Bismuth minerals, generally in very minor quantities, have been reported in many gold-quartz veins in the southern Piedmont gold belt, which extends from northern Virginia southwestward to Alabama in the southeastern part of the United States. These deposits are of general interest only.

Lead deposits from North Carolina to Maine contain 0.05 ppm to as much as 1 percent bismuth. The eastern lead deposits occur in the Appalachian Mountains and on the west side of the Adirondack Mountains in New York. All the deposits are in rocks that have been folded and faulted to a considerable extent. The host rocks include Precambrian dolomite on the west side of the Adirondacks, Precambrian or Cambrian schists in the districts east of the Blue Ridge in North Carolina and Virginia, lower Paleozoic dolomites west of the Blue Ridge in Tennessee and Virginia, Silurian conglomerates in southeastern New York, and both Precambrian granitic rocks and Triassic red beds and diabase in southeastern Pennsylvania. The Piedmont province is composed of Precambrian and highly metamorphosed Paleozoic rocks, relatively high in bismuth, whereas Triassic rocks are low in bismuth and high in antimony. Pegmatites in southeastern Pennsylvania and in western Maine commonly carry native bismuth and bismuthinite in small amounts.

The spatial proximity of igneous intrusive rocks to which the deposits can be related genetically varies from district to district. Deposits in the western Adirondack Mountains are associated with Precambrian granite intrusives, and those east of the Blue Ridge occur near batholithic masses of granite to which a Devonian or late Paleozoic age has been ascribed.

Native bismuth and other bismuth minerals are reported in placer gold deposits at many localities in Alaska and some localities in the southwestern and Rocky Mountain States. Bismuth minerals are said to be very abundant in the black sands in the Boise Basin district, Idaho, and some other localities, but bismuth is not known to have been recovered from these sources.

Bismuth is reported to occur in uranium veins in the Ralston Buttes district, Jefferson County, Colo., and native bismuth and emplectite ($CuBiS_2$) have been found in some deposits. A fairly clean hand-picked sample of pitchblende from the Schwartz-

walder mine reportedly contained 1.5 percent bismuth. Bismuthinite, native bismuth, and their oxidation products are reported in uraniferous veins in the White Signal and Blackhawk districts, New Mexico. Bismuthinite and molybdenite are reported in a vein containing brannerite in Mono County, Calif. A brannerite-rich mill product from Climax, Colo., also is reported to contain bismuth, which occurs in the range of 10–100 ppm in the Climax molybdenum deposit. No bismuth is known to have been recovered from uranium deposits in the United States.

The known bismuth deposits in Alaska are of minor importance and probably would not yield significant amounts of the metal. Vein deposits from which native bismuth and bismuthinite are reported include those along Charley Creek about 25 miles north of Nome; on Eva and Moose Creeks about 36 miles south of Nenana; on a headwater tributary of Fish Creek, about 15 miles northeast of Fairbanks; and along No Grub and Caribou Creeks in the Salcha River drainage. In these veins, native bismuth and bismuthinite are commonly associated with sulfide minerals, and with graphite and scheelite, in gold-quartz veins within igneous and (or) metamorphic rocks. The veins are generally less than 1 foot thick and commonly are localized by joint or foliation planes (Berg and others, 1964, p. 98; Cobb, 1970).

RESOURCES

IDENTIFIED RESOURCES

Measured, indicated, and inferred reserves of domestic recoverable bismuth associated with copper, lead, and zinc ores in Arizona, California, Colorado, Idaho, Montana, Nevada, New Mexico, and Utah are estimated at 26,400,000 pounds; in addition, potential bismuth resources in these ores are estimated at about 10 million pounds (Persse, 1970).

There is a potential resource of some 200,000 pounds of bismuth in domestic tungsten resources. However, only minor amounts of bismuth have been recovered from tungsten ores because the amount present seldom exceeds the maximum impurity allowance. Hence, its value would not offset the cost of recovery.

HYPOTHETICAL AND SPECULATIVE RESOURCES

The search for bismuth as an independent metal seems unfeasible because its association with lead, copper, molybdenum, tin, tungsten, and zinc will insure a bismuth supply, especially from the Western States.

Hypothetical bismuth resources may exist in smelter products. However, throughout the history of lead smelting few analyses have been made specifically for bismuth, and major smelting companies have analyzed only sporadically for bismuth. Analyses of bismuth in coal and coal ash indicate a source of bismuth, but only a few scattered occurrences have been noted. Data available indicate that certain coals may contain approximately 1 pound of bismuth in each 200 tons of coal. No technology has been developed for the removal of bismuth from coal or coal ash, and to our knowledge, no systematic studies are underway pertaining to the recovery of bismuth from coals.

PROSPECTING TECHNIQUES

Prospecting techniques that have had major roles in the discovery of new ore deposits, especially for copper, molybdenum, gold, silver, lead, and zinc, and indirectly for bismuth, are detailed geologic mapping, airborne and ground geophysics, geochemical exploration, drilling, and imagery. Probably little or no prospecting for bismuth has been done in the United States.

PROBLEMS FOR RESEARCH

The geology of bismuth, where it is known to occur with tungsten, molybdenum, oceanic manganese nodules, and coal, should be thoroughly investigated. In addition research needs to be done to ascertain potential bismuth resources in smelter products and coal ash and studies should be carried out on smelter byproducts to identify bismuth source areas in the United States.

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UNITED STATES MINERAL RESOURCES

BITUMEN-BEARING ROCKS

By W. B. Cashion

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ABSTRACT OF CONCLUSIONS

Bitumen-bearing rocks occur in many areas in the United States, but few deposits have been exploited or evaluated for their total energy potential. The evaluated deposits are a relatively small part of North American resources of bitumen-bearing rocks and probably will not contribute to U.S. energy needs before 1985. Studies of known but unappraised deposits, especially extensive subsurface tar sands, will greatly increase total resource estimates. Technological advancements are needed in tar-sand processing, especially for in situ recovery methods.

INTRODUCTION

Nonfluid petroleum occurs as interstitial deposits in numerous types of rock. These rocks and their associated hydrocarbons are commonly treated as one group, regardless of rock type, and have been referred to as tar sands, oil-impregnated rocks, asphalt-bearing rocks, oil sands, bitumen-bearing rocks, and petroleum-impregnated rocks. As used in this report, the term "bitumen-bearing rocks" is all-inclusive and, on the basis of information drawn from several reports, is defined as follows: Consolidated or unconsolidated rocks whose interstices contain viscous to semisolid to solid petroleum which in its natural state cannot be recovered by primary petroleum-recovery methods. This definition includes vein, dike, and asphalt-lake deposits as well as disseminated deposits, but it excludes pyrobitumens (such as coal and oil shale) and fluid bitumens.

Nonfluid bitumen occurs principally as disseminated deposits in small pore spaces spread throughout rock material. Bitumen content may be as much as 20–25 percent by weight but is normally much less. Bodies of homogeneous semisolid to solid hydrocarbon, containing very little rock material, occur in vein, pod, and lake deposits. These occurrences make up a small part of the total resource. Relatively small deposits can be developed, however, because of the purity of the ore.

Utilization of bitumen-bearing rocks in the United States has been chiefly in road building. Because of competition from refinery asphalt, the demand for native asphalt, supplied by bituminous sandstone and bituminous limestone, has not kept pace with the 20th-century surge in road construction. (See section "Exploitation.") Gilsonite is the only solid hydrocarbon produced in appreciable amounts. It is used in ink, paint, battery boxes, and numerous other manufactured items and is refined to produce high-quality coke and gasoline.

The Athabaska tar sands in Canada are being mined and processed by GCOS (Great Canadian Oil Sands, Ltd.) to produce crude oil. GCOS is producing about 45,000 barrels of oil per day, and they plan to increase production. Other companies also plan to add new installations.

In 1967, tar-sand deposits in Albania, Rumania, and Russia and an asphalt-lake deposit on the island of Trinidad were being exploited; in 1964 the La Brea, Trinidad, operation produced 189,246 tons of material (Phizackerley and Scott, 1967, p. 571).

The United States possesses a rather small part

of the world's resources of bitumen-bearing rocks. The in situ bitumen in all U.S. deposits that have been studied is here estimated to total a maximum of approximately 29 billion barrels (table 19). Numerous U.S. deposits need additional study. It should be noted, however, that any future estimate of energy in all bitumen-bearing rocks of the United States will probably be small compared to estimates for the remainder of the world. The estimate of world resources in major tar-sand deposits (those containing more than 15 million barrels of bitumen in situ) is 915.2 billion barrels (Phizackerley and Scott, 1967, p. 551).

Although substantial tonnages of tar sand in the United States are available for producing crude oil, there seems to be little incentive to develop the deposits in the near future. The National Petroleum Council, in its assessment of future energy supplies and demands, has predicted that Canadian deposits will be the primary and probably the only North American source of tar-sand oil through the year 1985 (Burk, 1971, p. 171).

EXPLOITATION

In many States, bituminous sandstone and bituminous limestone have long been mined commercially for use as road material, but currently there is activity at only a few places. The demand for asphalt, although it has increased greatly in recent years, is being supplied mostly by refinery asphalt. In 1968, bituminous limestone was produced in Alabama and Texas, and bituminous sandstone was produced in Kentucky and Missouri. During 1948–68, production of native asphalt and bitumens (bituminous sandstone, bituminous limestone, and gilsonite) increased from 1,136,126 to 1,786,840 short tons, and during the same period, there was approximately a threefold increase in production of refinery asphalt and road oil (Redfield and Spencer, 1950; Kirby and Moore, 1969).

Two basic production methods are used to recover the bitumen: (1) strip mining followed by extraction treatment and (2) in situ extraction. The first method recovers about 90 percent of the bitumen, and the second method 35–50 percent (Burk, 1971, p. 178). Mining and hot-water extraction method is being used in commercial development of the Athabaskan tar-sand deposits. The depths to which strip mining is feasible are limited, however, and deeper deposits will require in situ recovery methods. Experimentation with in situ recovery has had only limited success. Some nonfluid bitumen deposits contain appreciable amounts of sulfur and certain metals that may, with proper treatment, be recovered profitably.

Environmental problems that may be associated with a large-scale tar-sand development have not been studied extensively but in handling huge tonnages of material in a strip-mining operation some problems can be predicted, for example, water pollution, silting of streams, and unstable fill. In situ recovery has the advantage of not disturbing the surface, but the disadvantage of a lower bitumen recovery rate.

GEOLOGIC ENVIRONMENT

Nonfluid bitumen deposits occur most abundantly in sandstone and limestone, in lesser amounts in other types of sedimentary rocks, and rarely in igneous and metamorphic rocks (commonly adjacent to petroliferous sedimentary source rocks). Primary pore spaces in clastic rocks are host to more than 95 percent of the bitumen in deposits studied in detail. In secondary openings produced by weathering, solution, and structural movement, hydrocarbon deposits of gilsonite, ozocerite, and grahamite have been found. Gilsonite deposits in vertical veins in eastern Utah and western Colorado are the only sizable accumulations of solid hydrocarbons in the United States.

Sedimentary rocks containing bitumen represent a variety of environments of deposition, including marine, nearshore, and fluvial. Most of the large bitumen-bearing sandstone deposits occur in estuarine or fresh-water rocks (Phizackerley and Scott, 1967, p. 566), along basin margins where petroleum-bearing beds have been tilted and brought to or near the surface. Some bitumen-bearing rocks occur adjacent to faults, joints, unconformities, brecciated zones, and other geologic features which allow gases and light oil fractions to escape from accumulations of liquid petroleum.

The source and evolution of nonliquid bitumen evidently are not the same in all deposits. Studies of various deposits yield evidence to support all the following statements about the bitumen: (1) formed in situ, (2) migrated to present location, (3) a precursor of liquid petroleum, (4) a residue of liquid petroleum, (5) was deposited with the sediment, and (6) accumulated after deposition of sediments.

RESOURCES

Bitumen deposits in the United States are numerous and some individual deposits are extensive, but the fragmental information available does not

permit a detailed estimate of the total resources. Many deposits are characterized by extreme and abrupt vertical and lateral changes in bitumen content of the impregnated rock sequence. Evaluation requires closely spaced surface and subsurface data points, but in many areas it is not feasible to gather such data. Thickness, percentage of bitumen, lateral extent, and other characteristics of most of the deposits are poorly known. The larger deposits for which estimates have been made are given in table 19. Appraisal of other known deposits will result in

TABLE 19.—*Deposits of bitumen-bearing rocks in the United States with resources of at least 1 million barrels*

[Sources of data: Ball Associates, Ltd. (1965); Burk (1971)]

Age	Name of deposit	Type of deposit	Bitumen resources (millions of barrels, rounded)
California			
Late Miocene and early Pliocene.	Edna	Sandstone	141–166
Do	South Casmalia	Diatomaceous mudstone and vein deposits.	46
Do	North Casmalia	do	40
Pliocene	Sisquoc	Sandstone	26–50
Miocene	Santa Cruz	do	10
Pliocene and Pleistocene.	McKittrick	do	5–9
Miocene	Point Arena	do	1
Kentucky			
Pennsylvanian	Kyrock area	Sandstone	18
Do	Davis-Dismal area	do	7–11
Do	Bee Spring area	do	8
New Mexico			
Triassic	Santa Rosa	Sandstone	57
Texas			
Cretaceous	Uvalde	Limestone	124–141
Utah			
Permian and Triassic	Tar Sand Triangle	Sandstone	10,000–18,100
Eocene	P. R. Springs	do	3,700–4,000
Do	Sunnyside	do	2,000–3,000
Triassic	Circle Cliffs	do	1,000–1,300
Cretaceous and Oligocene.	Asphalt Ridge	do	1,000–1,200
Jurassic	Whiterocks	do	65–125
Eocene	Hill Creek	do	300–400
Do	Lake Fork	do	15–20
Do	Raven Ridge	do	100–125
Do	Rim Rock	do	30–35
Total			18,693–28,862

an appreciable increase in the estimate of total resources. Collation of information from exploratory wells in the Rocky Mountain States that are known to contain extensive subsurface tar-sand deposits will add a major segment to the resource estimate.

The major tar-sand deposits of the world (those with more than 15 million barrels of bitumen in situ) are estimated to contain 915.2 billion barrels of bitumen, of which about 710 billion barrels is attributed to Canada and 200 billion barrels to eastern Venezuela (Phizackerley and Scott, 1967, p. 551). Some other authors estimate that the eastern Venezuelan tar-sand resources are comparable to those of Canada, and Burk (1971, p. 174) mentioned that although deposits in Colombia have not been well defined, available information suggests the possible presence of almost a trillion barrels of bitumen in situ. Phizackerley and Scott (1967 p. 570) stated that very little information is available concerning Russian tar sands, but that one Siberian deposit reportedly contains impregnated Permian sandstone in an area the same order of size as the Athabaskan deposits.

Numerous reports deal with bitumen-bearing rocks in the United States, but few of these give data that can be used for resource estimates. Ball Associates, Ltd. (1965), in a survey of available data, listed 546 occurrences of bitumen-bearing rocks in 22 States, but scant data permit estimates of partial resources for only seven States. Readers who want details of individual deposits should consult the report of Ball Associates, Ltd. (1965) and a comprehensive annotated bibliography by Mullens and Roberts (1972). Brief descriptions of some of the more significant near-surface deposits, taken mostly from the report of Ball Associates, Ltd. (1965), follow.

Alabama.—Bitumen is found in several beds of sandstone and limestone of Mississippian age within a northwest-trending band, about 70 miles long and 8 miles wide, that extends across six counties in the northwestern part of Alabama. Some impregnated beds are as much as 20 feet thick, although most are less than 12 feet thick. Bitumen contents of as much as 15 percent by weight have been reported for assayed samples. The Alabama Geological Survey is studying the deposits.

Alaska.—Many bitumen-bearing rocks and oil seeps in Alaska have been reported, but owing to the nature of the terrain and structural deformation, little is known of the extent or thickness of impregnated beds.

California.—Nearly all bitumen deposits in California occur near the margins of sedimentary basins in rocks of Miocene and Pliocene age. The deposits are concentrated in the southwestern part of the State within 75 miles of the coast. Large tonnages are available in San Luis Obispo, Santa Barbara, Santa Cruz, and Kern Counties. In San Luis Obispo and Santa Barbara Counties, large deposits have been investigated for oil-mining possibilities, but

thus far none have been developed commercially. In California, the bitumen resources in only seven deposits, the largest being in the Edna district, San Luis Obispo County, are about 300 million barrels.

Kansas.—The principal deposits of bituminous rocks in Kansas are in the east-central and southeastern part of the State and are of Pennsylvanian age. The bitumen is in beds of porous sandstone and limestone in a stratigraphic sequence exposed across several counties in a band 15–40 miles wide. A core from an area in the southeastern part of the State shows a bitumen-impregnated sandstone 100 feet thick containing 65,000 barrels of oil per acre in situ.

Kentucky.—In west-central Kentucky sizable deposits of bitumen-bearing rocks occur, and in a few counties of eastern Kentucky minor accumulations occur. The asphalt-bearing strata are predominantly sandstone of Pennsylvanian and Mississippian age and have reported bitumen content of as much as 10 percent by weight. Estimates of bitumen resources for three areas in Kentucky are given in table 19.

Missouri.—Known deposits of bitumen are widely distributed in 21 counties in western Missouri. The deposits occur in both sandstone and limestone of Mississippian and Pennsylvanian age, but mostly in Pennsylvanian sandstones. The impregnated rocks of Mississippian age are mostly limestones located in the zinc-lead mining area in the southwestern part of the State. Maximum reported thickness of impregnated rocks is 30 feet, and maximum bitumen content is 15 percent by weight. No bitumen resource estimates have been made for Missouri, although some deposits are known to be extensive.

New Mexico.—One economically important tar-sand deposit occurs in New Mexico, and that is in the Santa Rosa Sandstone (Triassic) in Guadalupe County. The bitumen-bearing zone is as much as 60 feet thick and contains as much as 8 percent hydrocarbon by weight. A resource estimate for the Santa Rosa Sandstone is given in table 19.

Oklahoma.—Ball Associates, Ltd. (1965, p. 227–231) listed 80 areas containing petroleum-impregnated rock located in 21 Oklahoma counties. The largest deposits are in sandstones and limestones of Ordovician age in Murray County. The sandstone contains as much as 14 percent bitumen by weight. Other bitumen deposits are found in rocks ranging in age from Ordovician to Cretaceous.

Texas.—Cretaceous rocks, in a northeast-trending area that extends across the middle one-third of Texas, contain most of the known bitumen deposits of the State. The largest deposits, in the Uvalde district (table 19), are in the Anacacho Limestone. The bitumen-bearing sequence is as much as 200 feet thick, and its maximum hydrocarbon content is 20 percent by weight.

Utah.—Outcrops of tar sand are found in many sections of eastern Utah. The largest outcrops are situated around the margin of the Uinta Basin and in a triangle-shaped area west of the confluence of the Green and Colorado Rivers. The deposits in the Uinta Basin are, for the most part, in rocks of Tertiary age. Some impregnated zones extend through several hundred feet of sandstone and related rocks. Asphaltic zones in the "Tar Sand Triangle" are extensive and are as much as 250 feet thick. They occur in rocks of Permian and Triassic age. The estimate of nonfluid bitumen in Utah has been greatly increased as a result of recent studies by the Utah Geological and Mineralogical Survey.

Gilsonite is the only solid hydrocarbon produced in appreciable quantities. Utah has all the major deposits. The deposits are not large enough, however, to contribute greatly to the total energy needs of the United States. Original reserves of gilsonite are estimated to have been 45 million tons, and much ore has been mined from the widest veins. All operating mines are in Utah.

PROSPECTING TECHNIQUES

Discovery of most of the larger known occurrences of bitumen-bearing rocks has been due to visible indications of impregnations, such as discolored rocks and tar seeps. Other deposits have been found as a result of mineral-mining operations and exploratory drilling for oil and gas. Because there has been no rapid depletion of known tar-sand deposits, little attention has been given to developing sophisticated tools for prospecting. If the need arises for tar-sand exploration, some methods now employed in searching for liquid petroleum could be adapted to prospecting for nonliquid bitumen. In the near future, however, increases in the estimated amount of United States tar-sand resources will probably be a result of investigations of known deposits that have not been evaluated.

PROBLEMS FOR RESEARCH

Large reserves of relatively high-grade material occurring in a small area are required for large-scale economic development of bitumen-bearing rocks. In North America, the Canadian tar sands are, by far, the deposits best suited for exploitation. Development of the Canadian deposits has brought great advancement in the technology used in mining and processing enormous tonnages of tar sand, but

thus far the operation has had marginal economic success.

Most in situ recovery experimentation has not been encouraging. Variations in bitumen content, physical properties, and water saturation of the rocks cause problems in establishing and maintaining proper underground communication and flow rate.

Additional research is needed for improving in situ recovery methods and for determining those measures required to protect the environment during tar-sand development. Special attention should be given to deposits in arid climates inasmuch as a limited water supply could affect all phases of the development.

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CADMIUM

By Helmuth Wedow, Jr.

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ABSTRACT OF CONCLUSIONS

Cadmium, a trace metal similar to zinc in many ways but having a much lower crustal abundance, occurs as an impurity in zinc-bearing minerals. It is used chiefly in the electroplating of fabricated steel products to obtain superior corrosion resistance; additional uses are in the manufacture of yellow and red pigments, vinyl plastics, phosphors for television picture tubes, and nickel-cadmium batteries. None of the few independent cadmium minerals currently known is sufficiently abundant to be mined as an ore. thus, all cadmium produced has been as a byproduct of zinc refining from sphalerite. World zinc concentrates are estimated to contain an average of about one-fourth of 1 percent cadmium, of which about 75 percent is generally recovered or can be recovered during zinc smelting and refining.

Estimates of world cadmium resources place recoverable identified resources at more than 1.2 million metric tons, of which about one-fourth is in the United States. Total world recoverable and subeconomic resources, both identified and undiscovered, are estimated to be in excess of 18 million metric tons of contained cadmium. About one-sixth of these resources is in deposits believed to be exploitable under existing economic conditions.

Many of the deposits containing the world's cadmium resources are the conventional zinc-bearing types, chiefly those known as massive sulfide and strata-bound. However, significant low-grade resources occur in phosphorites and such black metal-rich shales as the Kupferschiefer of central Europe, in which the Cd:Zn ratio is considerably higher than in the more conventional deposits.

INTRODUCTION

Cadmium is a silver-white soft, malleable metal, which with its compounds has a wide range of industrial uses. Its relative rarity and consequent high price, however, have prevented more extensive use inasmuch as it is in direct competition with its more abundant less expensive sister element, zinc. Cadmium metal has a specific gravity of 8.65, and its melting and boiling points are 321°C and 765°C, respectively. The high luster on a freshly cut surface dulls rapidly with the formation of a thin, impervious coating of cadmium oxide, which is the most important characteristic of its use as a metal. All new commercial cadmium is obtained as a byproduct of zinc production, in which it is recovered from the fumes released by the roasting of zinc sulfide ores or from sludges generated during the purification of the sulfuric acid leachate of roasted zinc ore. Thus, most zinc producers also market cadmium.

Cadmium is available in several forms. It can be cast as balls, ingots, slabs, and other shapes, and also can be obtained as sticks, flakes, or sponge. Some producers also convert the molten metal directly to the oxide. For electroplating (see below) as much as 0.05 percent lead and 0.033 percent zinc is permitted, whereas for certain other uses the allowable maxi-

mums of zinc and lead are less. In addition, cadmium used in pigments requires a low content of thallium, and cadmium solders cannot contain even trace amounts of aluminum.

The major use of cadmium is in the electroplating of fabricated steel products to give them superior corrosion resistance. Such electroplating uses about 50 percent of the available metal. The metal is also used in low-melting-point alloys. The chief use of cadmium compounds is as pigments; cadmium sulfide, cadmium sulfoselenide, and lithopone generally account for the color range of yellow, orange, and red in corrosion-resistant paints. Cadmium stearate is used as a stabilizer in the production of some of the vinyl plastics. Cadmium phosphors are used widely in black-and-white television and as coatings for fluorescent tubes; these phosphors are also increasingly being used in color television for blue and green components. Cadmium nitrate is one of the chief components of the nickel-cadmium battery. Despite a variety of substitutes, cadmium is sufficiently superior to warrant continued use, and therefore most available supplies will be consumed. (See Heindl, 1970.)

EXPLOITATION

The industrial use of cadmium dates from the 1870's, although the metal was first detected as an impurity in zinc ores as early as 1817. All commercial cadmium used in the latter part of the 19th century was produced from the ores of the Upper Silesian zinc-lead district, at that time in Germany but after World War I in Poland. The cumulative German, and hence total world production, in the 19th century amounted to about 115 mt (metric tons). The United States first began to extract cadmium from zinc ores of the Joplin district, Missouri, in 1906 and since then has produced more than 150,000 mt of this metal. Total world production of cadmium thus far in the 20th century has exceeded 320,000 mt. The annual world production rate was 3½, 13½, 3,150, and 16,000 mt in 1882, 1900, 1935, and 1970, respectively. In comparison, the U.S. annual production rate was 6, 112, 1,800, and 4,300 mt in 1907, 1917, 1935, and 1970, respectively.

Because cadmium is recovered as a byproduct during the smelting and refining of zinc, its production is clearly a function of zinc production. (See chapter on "Zinc.") However, because cadmium is recovered at the smelter, world production more closely parallels zinc smelter production than mine production. Comparison of zinc production data with cadmium production data shows that the world has doubled its use of cadmium in the last 15 years, whereas its consumption of zinc has required about 20 years to double. This somewhat greater increase in the rate of cadmium production relative to that of zinc is due to the improvement of zinc-refining techniques and to the development of more efficient recovery methods. At the same time, some major zinc production has been shifted to ores somewhat richer in cadmium, as for example those of the Mississippi Valley type. These relations are clearly seen in shift of the Zn:Cd ratio of production data from values of more than 80,000 in the 1880's (the first decade of cadmium production) down to an average of about 525 for the 1930's, 340 for the 1940's, 350 for the 1950's, and 310 for the 1960's. From the ratio for the 1960's (310) and on the assumption that the average zinc-bearing concentrate contains 55 percent zinc and that about 75 percent of cadmium in the concentrate is recovered, it is estimated that world zinc concentrates average about 0.24 percent cadmium.

GEOLOGIC ENVIRONMENT

GEOCHEMISTRY

Cadmium is the chemical element with atomic number 48. Cadmium has an atomic weight of 112.41, and eight stable isotopes in proportions as follows:

Isotope	*Percent*
Cd^{108}	1.22
Cd^{109}	.88
Cd^{110}	12.39
Cd^{111}	12.75
Cd^{112}	24.07
Cd^{113}	12.26
Cd^{114}	28.86
Cd^{116}	7.58

Cadmium has a valence of +2 and an ionic radius of 0.97 Å. It belongs to Group IIb of the periodic system, along with zinc and mercury. Thus, cadmium is chemically very similar to these elements, a similarity that accounts for its relative concentration in zinc minerals despite a much larger ionic radius (0.97 Å versus 0.74 Å). However, cadmium is relatively more sulfophile than zinc and hence is relatively more concentrated in the later stages of magmatic differentiation and associated hydrothermal ores and even more so in the low-temperature reducing sedimentary environments. This relationship is clearly shown by the Zn:Cd ratios of various geologic materials given in table 20.

MINERALS

There are relatively few independent cadmium minerals. The native metal is unknown, and natural cadmium oxide (CdO) has been found only in Sardinia, as a coating on hemimorphite. Cadmium sulfide (CdS) occurs both as hawleyite, the cadmium

TABLE 20.—*Zinc and cadmium contents and zinc:cadmium ratios in selected geologic materials*

Geologic material	Average metal content (ppm)		Zn:Cd ratio	Reference
	Zn	Cd		
Crustal abundance	91	0.2	455	Zn—"Crustal Abundance," this volume; Cd—Parker, 1967.
Do	40	.15	270	Tourtelot and others, 1964.
Igneous rocks	132	.15	880	Rankama and Sahama, 1950.
Do	------	-------	530	Sandell and Goldich, cited by Rankama and Sahama, 1950.
Magmatic sulfides	8,500	20	425	Rankama and Sahama, 1950.
Swedish sphalerites	544,000	1,700	320	Gabrielson, cited by Rankama and Sahama, 1950.
Estimated average world zinc concentrate	550,000	2,400	230	"Zinc," this volume.
Joplin sphalerites	579,600	3,580	162	Siebenthal, 1909.
Southeastern U.S. sphalerites	609,000	5,200	117	Maher and Fagan, 1970.
Permian phosphatic shale, Wyo	10,400	200	52	Love, 1961.
Bentonites in Pierre Shale	110	2.8	39	Tourtelot and others, 1964.
Black shale	------	-------	10–30	Davidson, cited by Tourtelot and others, 1964.
Kupferschiefer ore, Mansfeld district	9,000	500	18	Cissarz and Moritz, cited by Rankama and Sahama, 1950.

analog of isometric sphalerite, and as greenockite, the cadmium analog of hexagonal wurtzite—sphalerite and wurtzite are the two crystalline varieties of zinc sulfide (ZnS). The anhydrous carbonate ($CdCO_3$), otavite, is the cadmium analog of smithsonite ($ZnCO_3$) and can occur as oriented overgrowths on zinc carbonate crystals. Otavite was first found at Tsumeb, near Otavi, South West Africa. The most common of the independent cadmium minerals is the sulfide, greenockite. It occurs chiefly as a yellowish earthy film or coating on zinc minerals, mainly sphalerite, and rarely as crystals. These coatings form as a result of the low-temperature alteration of sphalerite, chiefly alteration due to weathering.

ORES

None of the independent cadmium minerals is abundant enough to be an ore mineral, although the presence of trace greenockite in slightly altered or oxidized sphalerite will slightly enhance the cadmium content of the zinc-bearing ores. The chief source of commercial cadmium is zinc ore, and cadmium is by far the major metallic byproduct recovered in the smelting of zinc concentrate and the refining of zinc metal. Thus, the major concentrations of cadmium reasonably well known today are in the sulfide zinc ores, although potential resources exist in other zinc ores and in other lesser known potential zinc concentrations. (See chapter on "Zinc.")

The cadmium content of sphalerite is highly variable. This zinc sulfide, along with wurtzite, generally contains from less than 0.1 percent to 1 percent Cd and locally as much as several percent. The world average for zinc concentrates, which are dominantly sphalerite, is estimated as 0.24 percent Cd in material containing 55 percent Zn (table 20). The range and average cadmium content of sphalerites from selected U.S. and Canadian zinc mines and a few other occurrences of significance are listed in table 21. Higher temperature sphalerites appear to contain less cadmium than those formed at lower temperatures. Some of the lower cadmium values may also be due to metamorphism—that is, cadmium is mobilized and more widely dispersed preferentially to zinc during metamorphism of a preexisting sulfide deposit.

RESOURCES

Cadmium resources are closely associated with zinc resources. If the Zn:Cd ratio of 455:1 based on crustal abundances of these elements (table 20) is valid, then the amount of cadmium in the uppermost 1 kilometer of the continental crust of the earth is about 750×10^9 mt of which about 44×10^9 mt is within this depth in the United States. Erickson (See chapter on "Crustal Abundance") estimates world and U.S. zinc reserve potentials as $3{,}400 \times 10^6$ and 198×10^6 mt, respectively. If Erickson's zinc potentials are presumed to be chiefly in conventional sulfide ores, then similar cadmium reserve potentials, based on a Zn:Cd ratio of 230 for world zinc concentrates (table 20) can be estimated as approximately 15×10^6 and 0.86×10^6 mt for the world and the United States, respectively.

Estimates of cadmium resources for the United States and the world for this report are listed in table 22. These estimates were prepared chiefly by

TABLE 21.—*Cadmium content, in percent, of sphalerite from selected U.S. and Canadian mining districts and regions*

Location	Number of analyses	Range	Average	Reference
Balmat-Edwards, N.Y	13	0.08–0.15	0.12	Lenker, 1962.
Edwards, N.Y	1	--------	.4	Warren and Thompson, 1945.
Franklin, N. J	1	--------	.15	Lenker, 1962.
Friedensville, Pa	1	--------	.05	Callahan, 1968.
Do	1	--------	.20	Warren and Thompson, 1945.
Birmingham, Pa	3	.08– .16	.12	Lenker, 1962.
Valzinco, Va	1	--------	.22	Maher and Fagan, 1970.
Timberville, Va	2	.25– .38	.32	Lenker, 1962.
Do	2	.45– .60	.52	Maher and Fagan, 1970.
Austinville, Va	12	.13– .18	.15	Lenker, 1962.
Austinville (and other occurrences in Cambrian rocks of southeastern U.S.).	11	.08– .45	.18	Maher and Fagan, 1970.
East Tennessee, Kingsport ores	6	.24– .48	.32	Lenker, 1962.
Do	6	.25– .80	.47	Maher and Fagan, 1970.
Ducktown, Tenn	1	(1)	.09	Do.
Middle Tennessee veins	6	(2)	1.3	Jolly and Heyl, 1968.
Middle Kentucky veins	37	(2)	1.34	Do.
Illinois-Kentucky fluorspar district	5	.38–1.40	.69	Hall and Heyl, 1968.
Upper Mississippi Valley	6	.04– .40	.17	Do.
Tri-State	15	.11– .71	.34	Siebenthal, 1909.
Gilman, Colo	1	--------	.22	Lenker, 1962.
Rocky Mountain region (U.S. except Butte)	8	.1 – .6	.28	Kaiser and others, 1954.
Do	5	.4 –1.0	.58	Warren and Thompson, 1945.
Butte, Mont	3	.0X– .1	.1	Kaiser and others, 1954.
Do	3	.2 – .2	.2	Warren and Thompson, 1945.
Coeur d'Alene, Idaho	59	.10– .80	.40	Fryklund and Fletcher, 1956.
Metaline, Wash	2	.3 – .6	.45	Kaiser and others, 1954.
Northport, Wash	3	.1 – .7	.26	Do.
Western Canada, chiefly British Columbia	118	.2 – .9	.45	Warren and Thompson, 1945.
Ontario and Quebec	5	.2 – .3	.22	Do.
Pine Point, Northwest Territories	4	.06– .15	.11	Evans and others, 1968.

[1] Composite.
[2] Not given.

TABLE 22.—*Estimated identified and undiscovered cadmium resources of the United States and the world*

[Values given are in thousands of metric tons of contained cadmium]

	Identified resources	Undiscovered resources	Total resources
United States			
Recoverable	295	400	695
Subeconomic	---	---	1,500
Total	---	---	2,195
Rest of the world			
Recoverable	950	1,425	2,375
Subeconomic	---	---	14,000
Total	---	---	16,375
Total world			
Recoverable	1,245	1,825	3,070
Subeconomic	---	---	15,500
Total	---	---	18,570

applying Zn:Cd ratios of various geologic materials (such as those in table 20) to the basic data from which zinc resources were estimated. (See "Zinc," this volume.) The proximity of the estimate of recoverable cadmium resources in the United States (695,000 mt, in table 22) to the reserve potential (860,000 mt) suggests that the United States may be nearing its potential for cadmium associated with zinc ores as currently mined. On the other hand, the potential subeconomic resources, both identified and undiscovered, imply that there is no significant possible long-range shortage of cadmium from U.S. sources. The data in table 22 also indicate that world resources of cadmium, estimated at more than 18 million mt, are probably more than adequate for future needs as currently projected. One likely source for the future may well be marine phosphorites from which both zinc and cadmium could be extracted during the preparation of superphosphate fertilizers, although small amounts of these elements are undoubtedly needed in the final fertilizer product as trace nutrients.

Table 23 shows the distribution of recoverable identified cadmium resources of the United States by major geologic regions and compares these estimates with those for zinc in the same regions. Also given are the approximate Zn:Cd ratios for the respective zinc and cadmium recoverable identified resources of these regions. The Zn:Cd ratio of 150 for the total of these U.S. resources indicates that the greater part of this country's zinc ores are in mineral deposits that contain relatively more cadmium than the estimated world average (Zn:Cd ratio 230, table 20).

TABLE 23.—*Recoverable identified resources of cadmium in the United States, grouped by major geologic regions and compared with similarly classified zinc resources of these regions*

[See also chapter on "Zinc"]

Region	Zinc content of ores ($\times 10^3$ mt)	Approximate Zn:Cd ratio	Cadmium content of ores ($\times 10^3$ mt)
Appalachian	16,400	200	82
Mississippi Valley	19,200	120	160
Rocky Mountain	7,300	180	41
Pacific Coast	2,100	170	12
Total	45,000	[1] 150	295

[1] Average.

Because of the geochemical similarity of zinc and cadmium, most deposits containing zinc also contain cadmium but in lesser to barely trace amounts. As indicated previously, cadmium is produced solely as a byproduct of zinc extraction and purification. For detail on the types of zinc deposits, their classification, and the prospecting techniques used in the search for them the reader is referred to the discussion of zinc resources in "Zinc," this volume. For additional information on the utilization and exploitation of cadmium, the reader is referred to Heindl (1970).

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CHROMIUM

By T. P. Thayer

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ABSTRACT OF CONCLUSIONS

Although world reserves are large and resources of chromite ore are ample for the foreseeable future, domestic resources (excluding the national stockpile) are low grade and represent only about a 4- to 5-year supply. The outlook for substantially increasing domestic resources, even at several times present world prices, is not favorable. The thicker, minable parts of the Stillwater Complex in Montana, the principal domestic source, are complexly faulted and sheared off at depth. Although many podiform deposits must occur in serpentine along the Appalachian Mountains and Pacific Coast, most would be too small to mine at depths of 100 feet or more, even if means were available to locate them. A few relatively large podiform deposits probably are concealed at minable depths and might meet national needs for a few months at most.

The principal North American resources other than those in the Stillwater Complex are in a similar complex in Manitoba and very large low-grade deposits in Greenland. Metallurgical research to improve recovery of chromium from the low-grade "ores" and acquisition of more information on the Greenland deposits are needed. The only minable chromite reserves in the Western Hemisphere are a few million tons in Brazil and perhaps some in Cuba.

INTRODUCTION

Chromium is one of the most important and indispensable industrial metals. It is best known as a silvery white, hard, and bright metal plating on steel or other material used for decoration or protection from corrosion. Such coatings, however, rarely exceed 0.00002 inch in thickness and use only relatively minor amounts of the metal. Over the 5 years 1966–70, the United States consumed an average of 430,000 tons of chromium annually; about 67 percent was used in ferroalloys, about 18 percent in high-temperature furnace linings, and 15 percent in chemicals, including plating. In relatively small amounts, chromium hardens and toughens steel and increases its resistance to corrosion, especially at high temperatures. Most stainless steel contains about 18 percent chromium, and some cutting tools and wear-resisting alloys contain as much as 33 percent. The mineral chromite has some unique refractory uses. Although there are substitutes for chromium in many uses, such as titanium or aluminum for stainless steel and magnesite for chromite in refractories, no adequate substitutes have been, or are likely to be, found for chromium in some applications.

During the last 5 years, the United States has consumed about 7 million long tons of chromium ore, equal to about 28 percent of total world production, but it has mined none at all since 1962 (fig. 13). Our presumed resources are nearly all low grade; although theoretically they might last about 5 years at our present rate of consumption, they would be difficult to mine and expensive to use. Since 1962, our entire supply of chromite has been imported from the Eastern Hemisphere, and for the last 5 years about 45 percent of the chromium we have used in metallurgy has been imported from the Soviet Union.

EXPLOITATION

The alltime production of chromite in the United States is about 1,850,000 long tons; of this total about 950,000 tons, all high-iron ore and concentrates, came from Montana. The remaining 900,000 tons came almost entirely from podiform deposits in California, Oregon, Pennsylvania, Maryland, and Alaska. Since 1900, only in wartime has the United States produced more than 3,500 tons of chromite a year. During World War 1, the maximum domestic production of 82,430 long tons equaled less than half of consumption, and the gap between domestic production and consumption has widened ever since (fig. 13). Before 1940 all production was from podiform deposits, but since then, production of concentrates from the Stillwater Complex has predominated. Of 1,085,185 long tons produced during the Korean war for Government purchase programs, about 800,000 tons of Stillwater concentrates was stockpiled because of its low grade (38.5 percent Cr_2O_3). Moreover, despite a base price of $115 a ton for standard lumpy metallurgical ore during the Korean war, the podiform deposits as a group yielded only about 24,700 tons a year. From the period 1942–44 to the period 1952–57, an increase in price from $87 to $115 in 1954 constant dollars—a price increase of 32 percent—stimulated a rise in production of usable ore from podiform deposits by only 10 percent (Materials Advisory Board, 1959, p. 44).

Because the podiform deposits are small and most are in relatively inaccessible areas, no serious environmental problems are anticipated. Large-scale mining and milling operations at the Stillwater Complex, however, would entail large dumps and tailings ponds along the sides of a scenic part of the Stillwater River valley.

GEOLOGIC ENVIRONMENT

Chromium is a rock-forming element that is closely associated with magnesium and nickel in the ultramafic rocks peridotite, pyroxenite, and serpentine. From a normal range of 1,100–3,400 ppm (parts per million) and an average of about 1,800 ppm in ultramafic rocks, the content of chromium drops to about 200 ppm in gabbro and basalt, and 5 ppm in granite. Chromium is concentrated with the clay fraction of sedimentary rocks, normally in amounts of less than 100 ppm; but in phosphorites from Idaho, Wyoming, and Utah, it averages about 1,000 ppm (Michael Fleischer, written commun., 1972).

MINERALOGY OF CHROMITE AND CHROMITE ORES

The mineral chromite is the only commercial source of chromium and varies compositionally within wide limits permitted by the formula $(Mg,Fe^{2+})(Cr,Al,Fe^{3+})_2O_4$. The Cr_2O_3 content of the pure mineral chromite ranges from about 15 to 64 percent, but directly usable ores, which are mixtures of chromite and silicate minerals, range from about 33 to 55 percent Cr_2O_3. Compositionally, three general kinds of chromite ore are recognized: (1) high-chromium, which contains 46 percent or more Cr_2O_3 and has a Cr:Fe ratio of 2:1 or more; (2) high-iron, which contains 40–46 percent Cr_2O_3 and has a Cr:Fe ratio of less than 2:1; and (3) high-aluminum, which contains more than 20 percent Al_2O_3, and more than 60 percent Al_2O_3 and Cr_2O_3 combined. Although all three kinds are interchanged or blended for some uses, the high-chromium ores are used for metallurgy, and the high-aluminum ores mostly for refractories. Only high-iron ores are used for making chemicals, and they are also of major importance for making alloys and refractories.

All chromite ores consist of mixtures of chromite and associated minerals that are waste or gangue. Massive lumpy ore that contains little gangue is preferred by industry for metallurgical and refractory uses. Natural deposits, however, range from massive or high grade to disseminated or low grade, and ore commonly grades from one to the other. The low-grade ores may be concentrated by simple washing if they are friable or by grinding and separating the chromite from gangue by various physical methods. In general, milling of primary ores containing less than 10 percent Cr_2O_3 (20 percent chromite) has not been successful.

PRIMARY CHROMITE DEPOSITS

Primary chromite deposits occur only in certain kinds of ultramafic or closely related anorthositic rocks (Thayer, 1971) and are of two major geologic types: stratiform (layered) and pod-shaped (Jackson, 1961; Thayer, 1960, 1964).

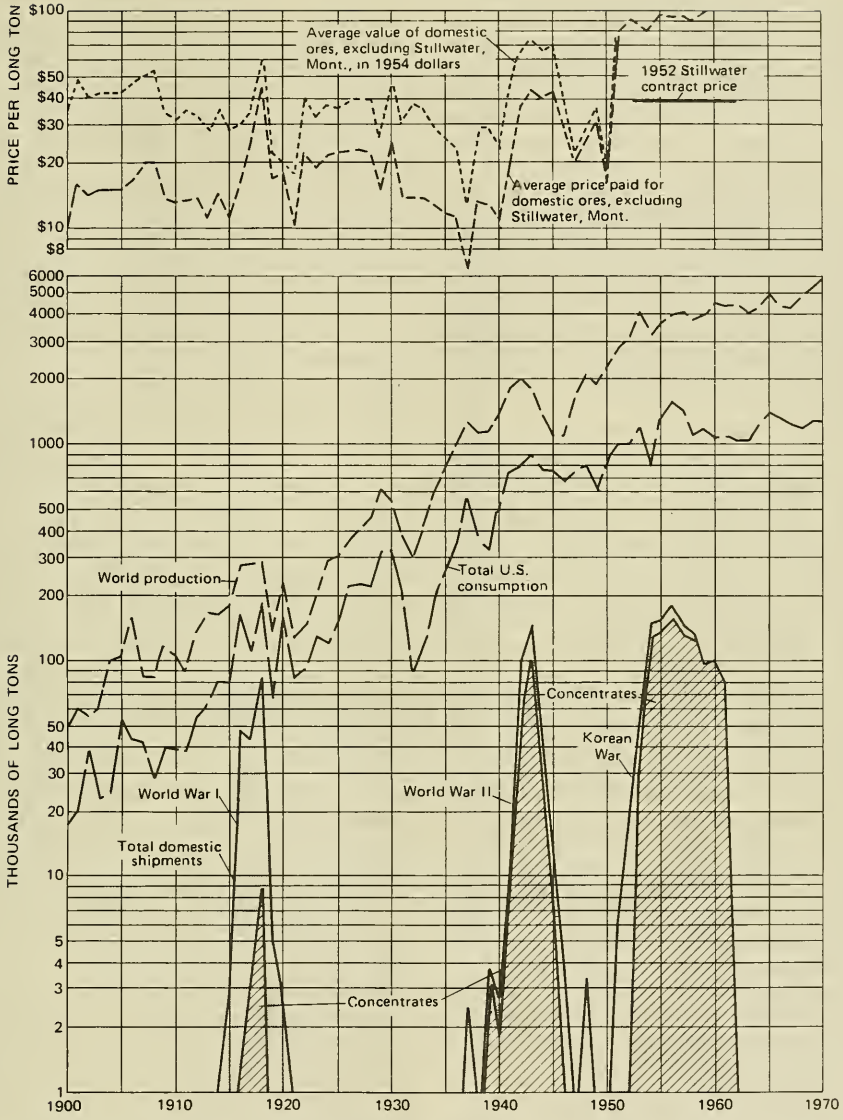

FIGURE 13.—World production and U.S. consumption and production of chromite ore and relation of price to domestic production from 1900 to 1970. Data from U.S. Geological Survey and from U.S. Bureau of Mines (1942–70).

STRATIFORM DEPOSITS

The stratiform deposits form layers in the lower parts of stratified igneous complexes of the Bushveld or Stillwater type; they are characterized by great lateral extent and uniformity and by consistent positions within the host complexes. They contain

more than 98 percent of the chromite resources of the world. The Steelpoort Main Seam in the Bushveld Complex in South Africa, for example, contains "reserves of merchantable ore conservatively estimated at half a billion tons" (Cameron and Desborough, 1969, p. 24). The chromite in stratiform deposits is predominantly of the high-iron type, but the high-chromium ores of the Great Dyke in Rhodesia are an outstanding exception. The regularity of the layering facilitates mining, even of thin seams, and is a reliable guide in prospecting. All the chromite-bearing layered complexes are geologically old, and in many the chromite layers have been dismembered by folding and faulting. Though mining may be difficult and expensive in highly deformed rocks, the layered structure usually can be used to guide exploration for sizable blocks of ore that have been separated.

The chromite deposits in the Stillwater Complex in Montana, which contains about 80 percent of the chromium resources of the United States, are of the layered high-iron type. They occur in an east-west belt about 30 miles long by half a mile wide. Thirteen chromite-rich zones are known; they range in thickness from 1 inch to more than 12 feet; several can be traced laterally more than 15 miles; and one can be traced more than 25 miles. The layers dip from about 50° to vertical and "extend downward to great depths except where terminated by major faults" (Jackson, 1963, p. 58). Two of the upper zones were mined in the eastern part of the complex under U.S. Government purchase contracts during World War II and the Korean war. In the Benbow mine nearly 65,000 long tons of concentrates averaging 41.5 percent Cr_2O_3 was recovered from a highly faulted vertical layer 4–5 feet thick (Materials Advisory Board, 1959, p. 42). In the Mountain View area about 830,000 long tons of concentrates averaging 38.5–38.8 percent Cr_2O_3 was recovered from two layered zones which range in width from 2 to 16 feet and from 3 to 8 feet, respectively (Price, 1963, p. 1).

Analogous to the Montana deposits are major deposits of the high-iron class in the layered Bird River complex in southeastern Manitoba, Canada. The complex has been folded to vertical and broken by numerous faults, and the probable total length of the chromite-bearing zone is 6–10 miles (Davies, 1958).

Extensive layered chromite deposits in anorthosite near Fiskenaesset in southwestern Greenland may represent the largest potential resources of chromite in North America. The chromite occurs in layered zones that average 1.5–10 feet in thickness, reach a maximum of 65 feet, and consist of interlayered anorthosite and chromitite layers, usually ¼–2½ inches thick. The chromite layers have a minimum exposed length of 75 miles. The chromite mineral averages about 33 percent Cr_2O_3, 0.9:1 in Cr:Fe ratio, and contains 0.2–0.5 percent V_2O_5, averaging about 0.3 percent. The average grade of rock in minable widths probably ranges from 15 to 25 percent Cr_2O_3. Although the rocks have been intricately folded, layers are favorably situated for mining over considerable areas. For example, it is estimated that one layer 3–22 feet thick along a strike length of 4,600 feet contains a million tons of recoverable chromite or 350,000 tons of Cr_2O_3 and 3,000 tons of V_2O_5. The chromite is exposed in completely bare outcrops near the coast; nearby fjords are deep, and Fiskenaesset harbor is accessible the year round (Ghisler and Windley, 1967).

The tremendous resources of chromite in South Africa and Rhodesia are in two great layered complexes, the Bushveld and the Great Dyke, respectively. The Bushveld Complex is a rudely basin-shaped layered mass 26,000 square miles in extent. As many as 29 chromite layers or groups of layers occur in various segments of the chromite-bearing zone, which is exposed over a distance of more than 70 miles along the eastern margin alone (Cameron and Desborough, 1969). Although some of the layers are less than 1 inch thick, several layers are of minable thickness and quality. The relation of ore reserves to geometry of deposits is illustrated by the Steelpoort Main Seam, mentioned earlier. If the inclined seam averages 40 inches in true thickness over a known distance of 40 miles and if the ore has a specific gravity of 4.2, each foot of ore below the outcrop represents 100,000 tons. In view of the 40-mile length, projecting only a mile downdip from the outcrop seems minimal but yields "half a billion tons" (Cameron and Desborough, 1969, p. 24). The total of 6.1 billion tons given for resources of the entire Bushveld Complex (Republic of South Africa) in table 24 is believed to be conservative.

The Great Dyke in Rhodesia is a layered complex 332 miles long by 3–6 miles wide. In cross section the Dyke is synclinal with dips of 20°–40° near the margins. Chromite layers occur over the entire length of the Dyke, and individual layers have been traced continuously the entire width, though they vary in number from 6 to 12 in different segments (Worst, 1960). The layers range in thickness from 2 to 18 inches, and nearly all the chromite is the high-chromium variety. Only layers 6 inches or more thick are mined below the outcrop; some of the thicker layers are mined more than 1,000 feet down the slope.

PODIFORM DEPOSITS

The podiform chromite deposits are lenticular or rudely tabular pods, but some defy description as to form. They range in size from a few pounds to several million tons. Most pod deposits yield less than 1,000 tons of ore each, but most of the production comes from ore bodies that contain 100,000 tons or more. Less than a dozen deposits that originally contained 1,000,000 tons or more are known. Most pod deposits are of the high-chromium type, but these deposits also are the only source of high-aluminum chromite. Podiform deposits occur in irregular peridotite masses or peridotite-gabbro complexes of the alpine type, which are restricted to mountain belts such as the Appalachians and Urals and to belts that surround most of the Pacific Ocean. Within many large complexes, the chromite deposits are localized, generally near contacts between peridotite and gabbro; but where there is no gabbro, deposits appear to be scattered at random.

Podiform chromite deposits are scattered along the Pacific Coast of the United States from the Kenai Peninsula in southern Alaska to southern California and along the Appalachian Mountains from northern Vermont to Georgia. The principal concentrations of deposits or districts are in the Klamath Mountains in southwestern Oregon and northern California, in the western slopes of the Sierra Nevada, in the Coast Ranges of California, in eastern Oregon, and in the Maryland-Pennsylvania (State Line) district (Thayer and Miller, 1962; Thayer, 1966; Thayer and Ramp, 1969). The largest single high-grade ore body probably was at the Woods mine in Pennsylvania, which yielded between 100,000 and 200,000 tons of lump ore before 1900 (Pearre and Heyl, 1960). Statistical analysis of recorded production from 456 mines in the United States between 1916 and 1953 has shown that of 517,000 long tons of ore shipped the largest 20 mines provided about 72 percent, 42 mines yielded 15.7 percent, and 394 mines yielded only 12.3 percent of the ore. These figures are believed to typify podiform deposits, and accordingly, they show that most deposits of this type are economically insignificant.

The high-chromium chromite ores of the Eastern Hemisphere, except for the Great Dyke, are mostly in podiform deposits that are concentrated in three major tectonic belts: (1) the Ural Mountains, (2) the so-called Tethyan mountain chains between the Alps and Himalayas, and (3) around the western margin of the Pacific Ocean. The largest single well-described deposit is the Coto ore body in the Philippine Islands (Stoll, 1958), which originally contained about 15 million tons of high-aluminum chromite ore. The Tiébaghi mine in New Caledonia and the Gölolan ore body in Turkey each yielded more than a million tons of high-chromium chromite. The southern Ural Mountains appear to include the greatest known concentration of large podiform deposits in the world, but no modern figures on size of deposits are available.

DISRUPTED STRATIFORM DEPOSITS

Tectonic disruption and dismemberment of stratiform deposits have led to misidentification of those in some districts as podiform. Recognition of parts of a once-continuous stratiform sheet can provide an economic incentive for systematic exploration to find missing segments, whereas a similar program in a podiform chromite district could be financially ruinous. No large podiform deposits are known in Precambrian rocks, and no true stratiform deposits are known in rocks younger than about middle Precambrian.

Recent cooperative investigations by the U.S. Geological Survey and the Companhia de Pesquisa de Recursos Minerais and Departamento Nacional da Produçao Mineral, under the auspices of the U.S. Administration for International Development, have revealed that the chromite deposits near Campo Formoso, Bahia, formerly believed to be isolated blocks actually are segments of a highly faulted layered complex 10 to 11 miles long. Massive layers that range from about 1 to 6 feet in thickness are of high-chromium (metallurgical) grade. Large amounts of high-iron chromite have been recovered by washing of disseminated ore that has been weathered irregularly to maximum depths of about 150 feet. Because a thick layer of debris from quartzite cliffs above the ore zone covers much of the area, the mines originally were located where this cover was thin. Determination by drilling that the deposits are semicontinuous under the debris has led to plans for production of 100,000–200,000 tons of ore a year (Mining Jour., 1972). Recent prospecting indicates that similar, although probably much smaller deposits, occur in the surrounding region. Podiform deposits, mostly of high-aluminum chromite, occur in small peridotite masses and in the Tocantins complex (Berbert, 1973; White and others, 1971) in central Goias along a north-south belt about 1,000 miles long. The lode deposits are small, and concentrations of residual chromite in soil have been the principal sources of production. Because exploration for chromite in Brazil is at an early stage, the estimates in table 24 are regarded as very tentative. The Bahia deposits are believed to have the largest minable reserves, by far, in the Western Hemisphere.

GENESIS OF PRIMARY CHROMITE DEPOSITS

All chromite of economic interest is believed to have been formed by crystallization from fluid magma essentially simultaneously with the associated silicates. Chromite and other minerals that crystallize early are denser than the magma, and the crystals, therefore, settle as they form and collect in layers on the floor of the magma chamber. In most stratiform complexes the layering and many delicate primary igneous and sedimentary features (Jackson, 1961) are preserved intact despite metamorphism and deformation. Many podiform deposits also preserve settled textures, some identical with those in the stratiform deposits, but also some that are unique (Thayer, 1964, 1969). The similarities of the podiform and stratiform deposits indicate a common origin by crystal settling, but differences between them are attributed to crystallization of podiform deposits in the upper mantle, and of stratiform deposits in the crust where they are now. Intrusion of peridotite and chromite from the upper mantle into the upper crust by solid flowage at high temperature, probably over distances of many miles, is believed to have fragmented the original layering and imposed metamorphic features on the podiform deposits and their host rocks (Thayer, 1969). Some features of chromite deposits that were interpreted 30–40 years ago as evidence of hydrothermal origin are now attributed to alteration of primary magmatic minerals.

SECONDARY DEPOSITS AND ASSOCIATED METALS

Erosion of chromite-bearing rocks may form secondary deposits of two kinds, black sands and lateritic soils. Because chromite is heavy and resists weathering, it may accumulate as grains in black sands or soil to form placers. Under favorable tropical or subtropical conditions, solution of magnesium silicates from ultramafic rocks by ground water forms lateritic soils which contain as much as 50 percent iron, 2–4 percent Cr_2O_3, 2–2.5 percent nickel, about a tenth as much cobalt as nickel, and some aluminum (Gross, 1970a, p. 27). Such ferruginous laterites are now being worked for nickel and cobalt in several countries and for iron ore in a few places, but economic recovery of the chromium has not been achieved. Chromite has been recovered from black sands in the United States and Japan on a relatively small scale, and from alluvial soil in Rhodesia by flotation on a large scale.

No other minerals are mined with primary chromite, although platinum occurs with layered chromite deposits in some complexes in the Ural Mountains. Some gold and platinum have been mined from chromite-bearing beach sands along the Oregon coast (Griggs, 1945), but no other minerals have been recovered during operations for chromite (Thayer and Ramp, 1969).

The second largest known chromium resource in the United States is in black-sand deposits in raised beaches along the southwestern coast of Oregon (Griggs, 1945). The black sand forms lenses and layers that range in thickness from a few inches to 42 feet and in width from a few tens of feet to more than 1,000 feet, and are as much as a mile long. Depth of overburden is as much as 75 feet of sand, clay, and gravel. The chromite is associated with ilmenite, rutile, magnetite, and heavy silicates, all of which are hard to separate because of similar physical properties. Zircon in the deposits is of definite economic interest. The explored deposits that contain 5 percent or more Cr_2O_3 approximate 2 million long tons. The concentrates would average about 40 percent Cr_2O_3, with a Cr:Fe ratio of 1.6:1.

RESOURCES

IDENTIFIED RESOURCES

A comparison of world production (fig. 13) and world resources of various categories (table 24) shows that chromite resources are ample for the foreseeable future. The only minable reserves in the Western Hemisphere, however, are in Brazil and Cuba. The figures for high-chromium chromite in the United States are postulated entirely on intensive exploration for extensions of known podiform ore bodies or new ore bodies in known districts under the stimulus of very high prices. Since 1918, mining of podiform deposits has been on a precarious basis; rarely have significant reserves been blocked out ahead of mining. The figures for high-iron presumed resources are based on an estimate of tonnages down to the level of the Stillwater River valley in the Stillwater Complex (Jackson, 1968) and in the Oregon black sands (Griggs, 1945). The Canadian and Greenland deposits are lower in Cr_2O_3 content and higher in iron than most Stillwater chromite. Western Hemisphere reserves (excluding the U.S. national stockpile) and presumed resources exclusive of Greenland total about 25 million tons, possibly a 12- to 15-year supply for the countries in the region.

Most of the Eastern Hemisphere resources is in the Bushveld and Great Dyke complexes in southern Africa, where labor is cheap and thin seams can be mined. The reserves of 1.05 billion tons for the Bushveld Complex are regarded as assured, although they have not actually been blocked out (Cameron and Desborough, 1969). The estimate of Rhodesian reserves is based mainly on layers of minable thickness

TABLE 24.—*Estimated world reserves and resources of chromite ore by type and country*

[Thousands of long tons of shipping ores and concentrates. A, high-chromium ore, Cr_2O_3 more than 45 percent, Cr:Fe more than 2:1. B, high-iron ore, Cr_2O_3 40–46 percent, Cr:Fe 1.5:1 to 2:1. B—, high-iron ore, Cr_2O_3 less than 40 percent. Cr:Fe 1.5:1 or less. C, high-aluminum ore, Al_2O_3 more than 20 percent, Al_2O_3 + Cr_2O_3 more than 50 percent; (C), amount not estimated. (S), layered or stratiform. (P), podshaped. (Pl), placer, subordinate. References cited are for subeconomic resources in the United States and for reserves in the rest of the world; all other estimates are extrapolated by the author from reserve figures and the geology of the deposits and are intended only to indicate possible order of magnitude of potential chromite resources]

	Type of ore and deposit	Identified resources [1]		Hypothetical [4] and speculative [5] resources	Reference and comments
		Reserves [2]	Conditional resources [3]		
WESTERN HEMISPHERE					
United States					
	A;(P)	None [6]	350	500	Modified from Thayer and Jackson (1957).
	B,B—;(S, Pl)	None [7]	5,000	2,000	
	C;(P)	None [6]	100	100	
Brazil					
	A;(S)	2,500	3,000 [8]	5,000	D. C. Hedlund, written commun., 1972.
	B;(S)	3,500	2,000		
	C;(P)	100	150		Estimate by author.
Canada					
	A;(P)		100		Davies (1958).
	B,B—;(S)		2,500	5,000	
Cuba					
	A;(P)		100?	1,000	Estimate by author
	C;(P)	250?	1,000?		
Greenland					
	B—;(S)		10,000	10,000+	Ghisler and Windley (1967).
Other					
			200	200	Estimate by author.
Hemisphere total	A	2,500	3,650	5,500	
	B	3,500		17,000+	
	B—		19,500		
	C	350	1,200	1,100	
	(other)		200	200	
Total		6,350	24,550	23,800+	
EASTERN HEMISPHERE					
Republic of South Africa					
	A;(S)	50,000	50,000	3,000,000+	Estimate by author.
	B;(S)	1,000,000	2,000,000		Cameron and Desborough (1969).
Rhodesia					
	A;(S, Pl)	500,0000	500,000	500,000+	Stanley (1961).
	B;(S)	50,000	50,000		Worst (1960).
U.S.S.R.					
	A;(P)	10,000?	10,000	25,000	Author's estimate.
	B—;(S)	1,000?	2,000		
	C;(P)	10,000?	10,000		

See footnotes at end of table.

TABLE 24.—*Estimated world reserves and resources of chromite ore by type and country*—Continued

	Type of ore and deposit	Identified resources [1]		Hypothetical [4] and speculative [5] resources	Reference and comments
		Reserves [2]	Conditional resources [3]		
Turkey					
	A,(C);(P)	5,000	5,000	5,000	U.S. Bur. Mines (1968, v. 66, no. 4, p. 6.)
Finland					
	B;(S)	10,000	5,000	10,000	Kujanpää (1971, p. 92).
India					
	A;(S,P(?))	5,000	4,000	20,000	Ratio of A:B estimated by author.
	B;(S)	2,000	2,000		Balasundaram (1972, p. 47).
Philippine Republic					
	A;(P)	700	500	1,000	Philippine Mining Yearbook (1971a, p. 26).
	C;(P)	4,000	2,000	5,000	Philippine Mining Yearbook (1971b, p. 54).
Malagasy Republic					
	A;(S?)	4,000	3,000	7,500	U.S. Bur. Mines (1966, v. 62, no. 6, p. 9).
	B;(S?)	1,000	2,000		
Iran					
	A;(P)	1,500	1,000	5,000	U.S. Bur. Mines (1968, v. 65, no. 2, p. 4–6).
Greece					
	A;(P)	50	100	250	Estimate by author.
	C;(P)	50			
Other					
	A,(C);(P) B;(S)	2,000	2,000	2,500	Estimate by author.
Hemisphere totals	A	577,250	574,550	3,581,250	
	B	1,064,000	2,060,000		
	B—	1,000	2,000		
	C	14,050	12,050		
Total		1,656,300	2,648,600	3,581,250	
World total (rounded)		1,663,000	2,675,000	3,600,000+	

[1] Identified resources: Specific, identified mineral deposits that may or may not be evaluated as to extent and grade, and whose contained minerals may or may not be profitably recoverable with existing technology and economic conditions.
[2] Reserves: Identified deposits from which minerals can be extracted profitably with existing technology and under present economic conditions.
[3] Conditional resources: Specific, identified mineral deposits whose contained minerals are not profitably recoverable with existing technology and economic conditions.
[4] Hypothetical resources: Undiscovered mineral deposits, whether of recoverable or subeconomic grade, that are geologically predictable as existing in known districts.
[5] Speculative resources: Undiscovered mineral deposits, whether of recoverable or subeconomic grade, that may exist in unknown districts or in unconventional form.
[6] Excludes chromite ores or equivalent in national stockpile: Metallurgical ore and ore equivalent. 4,760,000 long tons. Refractory (high-aluminum) ore, 1,050,000 long tons. Inventory of stockpile materials as of Mar. 31, 1972, U.S. General Services Administration.
[7] Excludes chemical chromite in national stockpile, plus concentrates stockpiled at Nye, Mont., 1,320,000 long tons total.

in the Great Dyke which have been projected to 500 feet below the surface but which are known to go much deeper (Stanley, 1961). Eastern Hemisphere reserves outside southern Africa are estimated at 55–60 million tons, and conditional resources at about 50 million tons. Even excluding southern Africa, reserves and presumed resources of the Eastern Hemisphere appear to be about triple those of the Western Hemisphere. However, because most of these resources are in podiform or highly deformed stratiform deposits, the uncertainties of supply and costs of production can be expected to mount rapidly as identified resources are depleted.

HYPOTHETICAL AND SPECULATIVE RESOURCES

The probability of finding major new chromite districts is believed to be shrinking rapidly, except possibly in central Asia, where little information is available. In the last 20 years, major high-chromium podiform deposits have been developed in two regions in Iran. The stratiform deposit at Kemi, Finland, with reserves of approximately 33 million tons of crude milling-grade high-iron ore, was discovered in 1959 (Kahma and others, 1962); it represents a major new district that was discovered under glacial drift. The low-grade but potentially very important chromite deposits at Fiskenaesset in southwestern Greenland were discovered in 1964 during regional geologic mapping (Ghisler and Windley, 1967). The figures for hypothetical and speculative resources are predicated more on discoveries in known districts than on new districts. The figures for India and Malagasy assume that large segments of disrupted stratiform deposits will be found in laterite-covered areas or at depth.

The universal presence of chromite as an accessory mineral in peridotite suggests a possibility of recovering it by large-scale mining of very low-grade rocks, as copper and molybdenum are mined from porphyry-type deposits. The analogy is not apt, however, for several reasons. In rock containing less than about 10 percent Cr_2O_3 or 20 percent chromite, because the chromite is fine grained and relatively soft, it slimes badly during the grinding necessary to free it from the silicates. Furthermore, flotation processes that work so well with sulfide ores present difficulties for chromite, an oxide (Batty and others, 1947; Sullivan and Stickney, 1960). Concentrates from low-grade disseminated ores normally are considerably lower in chromium and richer in iron than high-grade massive ores (Jackson, 1968, p. 1510).

Extensive deposits of iron-rich laterite blanket many peridotites in tropical and subtropical regions of the world. The laterite contains approximately 40–50 percent iron, 0.5–3 percent chromium, 0.2–2.5 percent combined nickel and cobalt, some aluminum, and 10–15 percent combined water (Gross, 1970a, p. 27). Only relatively small amounts of laterite are used as iron ore, although nickel is recovered from laterite on a large scale by hydrometallurgical processes in New Caledonia and Cuba. Recovery of all the metals presents difficult unsolved metallurgical problems. The laterites of Cuba alone have been estimated at 3 billion tons; at an average of 2 percent Cr_2O_3 (1.4 percent Cr), they would contain 42,000,000 tons of chromium metal (Gross, 1970b, p. 250). Estimates of the potential chromium resources in laterite are not included in table 24 because of the low tenor of chromium, scarcity of essential data on tonnages, and the lack of technology for recovery.

EXPLORATION FOR CHROMITE DEPOSITS

Restriction of chromite deposits to the lower parts of very distinctive layered complexes and to peridotite of the alpine type (Thayer, 1971) sharply limits areas for prospecting. By virtue of its resistance to weathering, massive chromite crops out or forms bouldery float and black sand that can be traced readily. In stratiform complexes the layered structure can be used as a guide to concealed deposits and faulted blocks or segments of ore.

Prospecting for concealed podiform deposits generally has been disappointing. In large peridotite-gabbro complexes, chromite deposits are concentrated within the peridotite near the gabbro, and thus the peridotite-gabbro contact can be used as a guide to the most promising ground (Flint and others, 1948; Rossman and others, 1959). Under almost ideal conditions of low relief in central Cuba, gravimeter surveys located some concealed deposits (Hammer and others, 1945), but in most areas high relief precludes use of this method. Magnetic surveys can outline areas of serpentine very accurately, but because most chromite is less magnetic than the host rocks, such surveys do not indicate concealed deposits. The high-iron stratiform deposits at Kemi, Finland, however, were traced under glacial till by a combination of magnetic and gravimetric surveys (Kahma and others, 1962). Seismic methods are not effective because most ore bodies are too small to detect and the host rock commonly is highly fractured and sheared. Known geochemical methods are not applicable because of presence of accessory chromite in all peridotite. With the exceptions noted, no substitute for detailed geological mapping and traditional means of underground exploration has been devised for finding concealed podiform chromite deposits.

PROBLEMS FOR RESEARCH

The fundamental problem of chromium supply for the United States is lack of domestic high-grade deposits and scarcity even of low-grade resources. Endeavors to expand the domestic resource base substantially would, it is believed, be very costly (Brantley, 1970, p. 260). Without access to South African, Rhodesian, and Russian sources, we would have to be prepared to depend largely on low-grade high-iron chromite ores from the Stillwater Complex, from Canada, and from Greenland. This would entail major shifts and inefficiencies in metallurgy and for most other uses.

Exploration for concealed podiform chromite deposits in the United States faces major problems and limitations. The first problem is the inability of known geophysical and geochemical methods to point to deposits concealed under very thin cover in areas of even moderate relief. The limitations are twofold: most podiform deposits are too small to be minable even at moderate depths, and in aggregate the few postulated relatively large deposits could only mitigate the national supply problem temporarily and at very high cost.

Research on means to recover more chromium from scrap and from low-grade ores appears more promising than geological research on domestic resources. Stainless-steel scrap, other than mill scrap, in 1968 provided the equivalent of 51,000 tons of chromium, or about 12 percent as much as was imported in ore (Brantley, 1970, p. 252). Recovery of chromium from scrap presumably will increase with development of processes to dispose of solid waste in general.

Development of processes to smelt the higher grades of Stillwater crude ore directly to FeCr alloy with local energy would avoid losses of 15–20 percent of contained Cr_2O_3 in milling (Thayer, 1962, p. 12) and could greatly reduce transportation costs to eastern consuming centers. Research aimed at adapting a process for direct smelting of high-iron chromite to stainless steel, announced in 1966 (Brantley, 1970, p. 261), to treat crude Stillwater ores, would seem to be indicated. Though such a process cannot compete with recovery of chromium from African ores at present prices, increases in wages of African miners to equitable scales and increased production of FeCr in southern Africa for export could change the situation drastically. Investigations of the Greenland ores should consider the likelihood of separating chromite readily from anorthosite by sink-float methods, and recovery of the contained 0.3 percent of V_2O_5 (Ghisler and Windley, 1967).

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CLAYS

By John W. Hosterman

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ABSTRACT OF CONCLUSIONS

Clays are naturally occurring rocks composed of fine particles that are principally hydrous aluminum (or magnesium) silicates. They occur as deposits that are divided for commercial purposes into kaolin, ball clay, fire clay, bentonite, fuller's earth, and miscellaneous clay. Resources of clay deposits similar to those used currently are extremely large, except for those of high-grade ball clay and high-grade colloidal bentonite. The geologic profession could be of better service to the city, county, and State planners, the clay producers, and the consumers of a wide variety of clay products if geologists doing areal geologic mapping, particularly near metropolitan areas, were more aware of the economic potential of clay occurrences in the area being mapped. Attaining such awareness may require the making available the necessary equipment and procedures to evaluate the economic potential of the clay occurrence.

INTRODUCTION

Clay was first used in the United States by the Indians for making pottery. It has been used extensively as the building material for adobe, a sun-dried mixture of clayey loam, straw, and water since the time of the early Spanish settlers in the southwestern part of the country. Clay was first used in this country in 1585 to make building brick at the Raleigh settlement on Roanoke Island, N.C. Dr. Danial Coxe, an early governor of West New Jersey, was probably the first to make pottery in the Colonies, when he built a plant at Burlington, N.J., about 1685. White clay is reported to have been first mined by the Indians in western North Carolina; and was exported to England in the early part of the 17th century.

Clays are naturally occurring rocks, both unconsolidated and consolidated, composed of very fine particles of clay minerals that principally are layered hydrous aluminum (or magnesium) silicates but may contain varying amounts of iron, potassium, sodium, and other ions. All deposits of clay contain other minerals, and these impurities are rare in some deposits but abundant in others. The most common other minerals are quartz, mica, feldspar, iron oxides, and carbonates. Titanium-bearing minerals and gypsum are abundant in some deposits; organic matter, such as carbon or kerogen, is abundant in others.

Most deposits of clay have as their major component, one of the following clay minerals: Kaolinite, halloysite, montmorillonite, palygorskite, and illite. Some clay deposits may contain one or more of these clay minerals as a minor constituent. The U.S. Bureau of Mines has classified clay deposits into

six categories both on the product rather than on the raw material. They are kaolin, ball clay, fire clay, bentonite, fuller's earth, and miscellaneous clay. Major difficulties are met in statistical records because different types of clay products are made from the same clay minerals. Kaolin, ball clay, and fire clay are composed chiefly of kaolinite, and all have the same properties, especially when fired. Bentonite consists primarily of montmorillonite. Fuller's earth may be composed of montmorillonite or palygorskite or both. Miscellaneous clay is composed of illite as the dominant mineral, particularly in the shales, but some deposits contain kaolinite and montmorillonite as the major constituents.

The structural formula of kaolinite is $(OH)_8Si_4Al_4O_{10}$, and its theoretical composition is 39.50 percent Al_2O_3, 46.54 percent SiO_2, and 13.96 percent H_2O. Other minerals of the kaolinite group are metahalloysite and its hydrated form halloysite. Metahalloysite has the same formula and composition as kaolinite, but halloysite contains two more molecules of water. Halloysite is more common than metahalloysite, but inasmuch as dehydration takes place at room temperature, halloysite converts irreversibly to metahalloysite which may be indistinguishable from kaolinite. Kaolinte is a potential source of aluminum because it contains as much as 39 percent alumina. Furthermore, some kaolin deposits contain gibbsite ($Al(OH)_3$), and some fireclay deposits contain diaspore ($AlO(OH)$) or boehmite ($AlO(OH)$), which increases the alumina content of these deposits to between 40 and 70 percent. (See "Aluminum.")

Kaolinite and halloysite are formed by hydrothermal, katamorphic (weathering in place), and sedimentary processes, either alone or in combination. Hydrothermal clay is formed by ascending hot solutions dissolving the country rock and precipitating a mineral of the kaolinite group. These clays are sometimes associated with sulfide deposits. Residual clay is formed in place by the action of chemical weathering, a katamorphic process that alters minerals such as feldspars and muscovites to kaolinite or halloysite. In general, the residual clays are well crystallized and coarse grained. Deposits of unconsolidated sedimentary kaolinite are formed by the weathered debris being eroded, transported by streams, and deposited in fresh- or brackish-water lakes and lagoons. The kaolin deposits contain large flakes of well-crystallized kaolinite, and the ball-clay deposits contain very fine flakes of poorly crystallized kaolinite and impurities of illite and (or) montmorillonite. The size and crystallinity of the kaolinite depend upon the source material, amount of breakup during transportation, and to some extent the amount of diagenesis or recrystallization after deposition. Deposits of consolidated sedimentary kaolinite are formed by the weathered debris being eroded, transported by streams, and deposited in swamps. After deposition, leaching by organic and carbonic acids removes iron, potassium, and other ions so that silica and alumina are concentrated, and then postdepositional diagenesis causes recrystallization of the kaolinite. Kaolinite formed in this manner occurs in deposits of fire clay or underclay which contain four types of clay differing primarily in the degree of crystallinity and the amount of impurities. The four types are plastic, semiflint, flint clay, and nodular flint. Plastic clay is composed of poorly crystallized kaolinite and contains illite as the major impurity; flint clay is composed of well-crystallized kaolinite and contains no impurities. Nodular flint clay is composed of well-crystallized kaolinite and contains diaspore or boehmite, because advanced leaching has removed some silica and has concentrated alumina.

Bentonite, by geologic definition, is a product of the devitrification and alteration of volcanic ash or tuff. The chemical alteration of the fine-grained ash that accumulated in a marine environment probably began while the ash was settling through the sea water. Most bentonites consist chiefly of montmorillonite $(OH)_4Si_8(Al_{3.34}Mg_{0.66})O_{20}$; however, some montmorillonite clays not formed from ash or tuff are still classified as bentonite under commercial usage of the term.

Fuller's earth produced in the Attapulgus, Ga.–Quincy, Fla. district is predominantly palygorskite (attapulgite), $(OH_2)_4Mg_5Si_8O_{20}\cdot 4H_2O$; most of the fuller's earth produced from deposits elsewhere in the United States is montmorillonitic clay, and several of these deposits are actually bentonitic clays. The origin of palygorskite is speculative, but the general agreement is that it formed in sea water that had a high content of magnesium and silica. Evidence from samples taken from the bottom of the Atlantic Ocean indicates that palygorskite can form as a chemical precipitate from the reaction of hydrothermal solutions with sea water.

Illite is the dominant mineral in the miscellaneous clay, especially in the shales, and its approximate formula is $(OH)_4K_2(Si_6\cdot Al_2)Al_4O_{20}$. Illite can be formed in many ways, but as the major constituent of shales, it is the result of weathered debris' being eroded, transported by streams, deposited in a near-shore marine environment, and subjected to diagenesis and lithification.

Materials such as talc, silica, and calcium car-

bonate can be substituted for many kaolin end products; however, the comparatively low cost of clays gives them a decided advantage over most substitutes. Many construction products and raw materials can be substituted very effectively for brick, tile, and lightweight aggregate. A few of the major ones are concrete, stone, glass, metal, plastics, expanded slag, sintered fly ash, vinyl asbestos, and cork.

In 1969, the United States produced 58,694,000 short tons of clay, exported 1,574,000 short tons, and imported 82,000 short tons (Wells, 1971, p. 287). The only clays imported in any large quantity were kaolin and ball clay, but all six types of clay were exported. Of the total clay production in 1969, miscellaneous clay accounted for 72 percent; fire clay, 12 percent; kaolin, 8 percent; bentonite, 5 percent; fuller's earth, 2 percent; and ball clay, 1 percent (fig. 14).

In the United States, clay resources consisting of material similar to that used currently are large, but the clay deposits included in such resources may not be ideally located for potential markets. Information on clay resources in the rest of the world is not complete, but undoubtedly these resources are enormous.

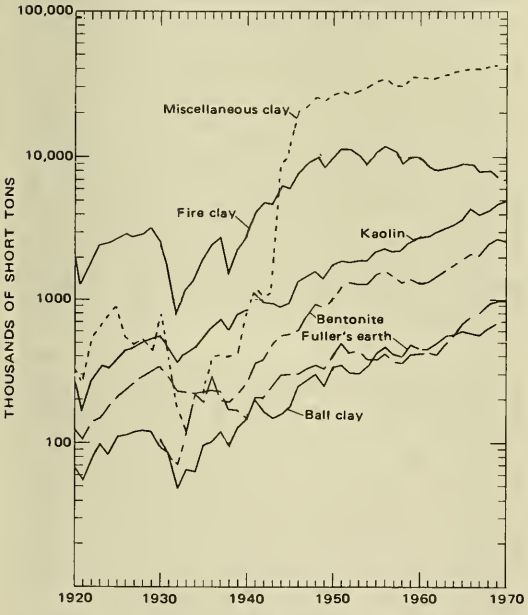

FIGURE 14.—Production of miscellaneous clay, fire clay, kaolin, bentonite, fuller's earth, and ball clay in the United States, 1920–70.

KAOLIN

The term "china clay" is somewhat synonymous with kaolin, particularly for the raw material used for ceramic products other than refractories. Kaolin is white and easily dispersible and can be fired at high temperatures without warping or changing color. It is used primarily for coating and filling paper, but other major uses are as fillers for products other than paper and refractories. Minor uses include pottery, dinnerware, stoneware, and white cement. Both kaolinite and halloysite are used in the petroleum industry as petroleum-cracking catalysts. Most kaolin is white, or nearly so, but shades of red, yellow, and brown are common. Most of it is plastic when wet, but some is hard and has flinty characteristics of homogeneity and conchoidal fracture. Although many kaolins are pure enough to be used in their natural state for many purposes, most kaolins are refined or are beneficiated by washing or by several other processes.

Five tons of kaolin was mined near Franklin, N.C., and shipped to Josiah Wedgewood in England in 1767–68. Since that time, the demand for kaolin has increased so greatly that in 1970 production reached almost 5 million short tons valued at slightly more than $100 million. Georgia and South Carolina are the major producers of kaolin, and small quantities are produced in Alabama, California, Florida, Idaho, North Carolina, Pennsylvania, Texas, and Utah. Kaolin production has increased at a nearly constant rate during the past 50 years (fig. 14). The depression in the 1930's and the recessions since then have affected kaolin production less than any of the other types of clay. The average value per ton has increased from $5.75 in 1933 to $21.91 in 1968. This undoubtedly indicates that increasing demands for high-quality clay used for paper filler and paper coater have caused production costs to rise steadily.

Reserves of kaolin in the Cretaceous and Tertiary rocks of the coastal plain of Georgia, Alabama, and Mississippi are estimated to be more than 300 million tons. Other deposits estimated to contain 1 million tons of kaolin are scattered throughout the Appalachian region. The Nation's resources of kaolin, which contain a much higher percentage of impurities than the reserves, are estimated to be at least 5 billion tons. This includes the potentially recoverable kaolinite and halloysite found in saprolite in North Carolina, California, Washington, and Idaho, and the hydrothermal halloysite in Utah and Nevada.

Byproducts—sand for use in making glass and muscovite for use in insulation and other products—are recovered from kaolin deposits in Latah County, Idaho, and muscovite is recovered near Spruce Pine, N.C., Sand for the glass industry is recovered from the kaolin deposit in Orange County, Calif. Bauxite is a minor byproduct of some of the kaolin deposits in the Coastal Plain of Georgia and Arkansas.

BALL CLAY

The term "ball clay" originates from an early English mining practice of rolling the highly plastic clay into balls weighing 30–50 pounds. The impurities found in ball clay are illite, montmorillonite, and carbonaceous matter. Quartz, as particles of silt and sand size, and iron oxide minerals are virtually absent from the best grade ball clays. The color of most ball clay is nearly white, but some colors range from pink to brown and through shades of gray to black. The color after firing is almost white. Ball clays require between 40 and 65 percent water of plasticity to become workable; plasticity, toughness, high dry-green strength, and adhesion are the outstanding characteristics of ball clay. When fired, ball clay becomes dense and vitreous, and its deformation point is between 1670° and 1765°C. Whiteware, floor and wall tile, and refractories account for most uses of ball clay, and building brick and paint filler account for minor uses.

Ball clay was first mined in the United States in 1860 near Paris, Tenn., but it was used only by the local pottery industry. Steady production of ball clay began in 1894 when Mr. I. Mandle shipped clay from western Tennessee to East Liverpool, Ohio. The production of ball clay in 1969 was 682,000 short tons valued at $9.7 million. Tennessee, Kentucky, and Mississippi are the major producers, but very small quantities are produced in Maryland, Texas, and California. Production of ball clay has been increasing during the past 50 years (fig. 14); however, during the depression years of 1921 and 1932–34, production was low, and the amount of ball clay produced yearly is lower now than any other clay commodity. The average value per ton has increased from $6.21 in 1933 to $14.25 in 1969.

Lenses of ball clay are known to occur in the following sedimentary units: Wilcox and Claiborne Formations of Eocene age in Kentucky, Ripley Formation of Cretaceous age and Wilcox and Claiborne Groups of Eocene age in Tennessee, Fearn Springs Sand Member of the Nanafalia Formation and Claiborne Group of Eocene age in Mississippi, Wilcox Formation of Eocene age in Texas, and Potomac Group of Cretaceous age in Maryland. All these units are located in the Coastal Plain and Mississippi Embayment, and most of the best grade ball clays are shipped from the Mississippi Embayment area.

Reserves of ball clay containing the lower percentages of quartz sand and silt are estimated to be about 4 million tons in Kentucky, Tennessee, and Mississippi. Resources of ball clay are estimated to be more than 50 million tons, but this total includes ball clay containing a percentage of sand and silt higher than that in the deposits now being mined.

FIRE CLAY

The term "fire clays" originated from their refractory property, the ability to be fired at high temperatures without warping. On the basis of their physical appearance, characteristics, and properties, fire clays can be divided into four categories: plastic clay, semiflint clay, flint clay, and nodular flint clay. The associated minerals are mainly quartz, siderite, feldspar, and rarely anatase. The color of fire clay, controlled primarily by the amount of carbonaceous matter, is mainly some shade of gray, but brown and black are common. The relative plasticity and hardness give a good indication of the refractoriness of each type. The flint and nodular clays have no plasticity and are the hardest and most refractory, deforming when fired at temperatures between 1,745° and 1,805°C. The plastic clay is the most plastic and the softest, and it deforms when fired at 1,620° to 1,670°C. Semiflint clay is intermediate in plasticity and hardness, and it deforms when fired at 1,670° to 1,745°C. The fired colors range from red to buff and gray. Fire clays are used in making refactories, structural brick, sewer pipe, pottery, stoneware, floor and wall tile, and cement and as fillers.

The first production of fire clay in the United States was in New Jersey where fire clay was mined at Woodbridge in 1816 for shipment to Boston, Mass., and the first plant for making refractory products was built in 1825 at Salamander, N.J. Until 1943, fire clay was the leading clay commodity (fig. 14), but since then, it has been second to the clays of the miscellaneous group. The demand for fire clay increased to a peak production of 11.8 million short tons in 1957, and since then production has steadily declined to 7.2 million short tons in 1969. This decline is due to the major change by the steel industry from open-hearth furnaces to basic oxygen furnaces. The production of fire clay

will probably continue to decrease in the future. The major fire-clay-producing States are Alabama, California, Colorado, Illinois, Kentucky, Missouri, Ohio, Pennsylvania, Texas, and West Virginia. The minor producers are Arizona, Arkansas, Idaho, Indiana, Kansas, Maryland, Minnesota, Mississippi, New Jersey, New Mexico, Oklahoma, Oregon, Utah, and Washington. The average value per ton was a low of $2.35 in 1942 and a high of $5.29 in 1967.

All deposits of fire clay are found in sedimentary rocks, and many of them are associated with coal beds. Much of the fire clay produced east of the Mississippi River is from the Lower Pennsylvanian sedimentary rocks; these clays are referred to as underclays because they almost invariably occur just below coal beds. Some kaolin called fire clay is mined from the Raritan Formation of Cretaceous age in New Jersey, from the Nanafalia Formation of Eocene age in Georgia and Alabama. West of the Mississippi River, fire clay occurs in beds and lenses of the Dakota Sandstone of Cretaceous age in at least six States. In Missouri, the clay is in the Cheltenham Clay of Wanless (1939) of Pennsylvanian age. In the Pacific Coast States and Idaho, fire clay occurs in Eocene sediments, the Ione Formation in California being the most productive.

The reserves of fire clay suitable for use in low- and moderate-heat-duty refractories are estimated at 1 billion tons, and for high-heat-duty refractories, flint and nodular flint clays, the reserves are estimated at about 500 million tons. Resources of fire clay are estimated at approximately 7 billion tons. If the future demands for fire clay decrease, the present production trend of fire clay will continue as shown (fig. 14); however, most of the decline will be in the demand for high-heat-duty refractory products, and the demand for low- and moderate-heat-duty refractory products will remain constant and may increase in the future as the production of metals expands.

In some areas where fire clay occurs as underclay, there is economic waste in the mining methods. Before World War II, almost all fire clay was mined by underground methods, and the coal was left because it made a better, safer roof than shale. Locally, the coal was mined from areas in the mine where the clay had been removed previously. Underground mining has become very costly, and for the past 10 years, fire clay has been almost exclusively strip mined. Now, the clay companies rarely mine any potentially economical coal as a coproduct, and the coal is wastefully placed on the spoil bank with the overburden by means of draglines, power shovels, and bulldozers.

BENTONITE AND FULLER'S EARTH

Bentonite and fuller's earth are clay commodities that are related either by mineral composition or by use. The term "fuller's earth" comes from its former use which was for cleaning or fulling wool by fullers. Both bentonite and fuller's earth have a wide variety of physical properties that make them suitable for many different uses and applications. Both are used in drilling muds, bentonite principally where fresh water is present in the rocks penetrated and palygorskite-type fuller's earth where salt water is present. The "sodium," "high swelling," or "Wyoming"-type bentonite has exchangeable sodium ions and when wetted with water will increase in volume 15–20 times. The "calcium," "low-swelling," or "southern" bentonite will not increase in volume when wetted with water. The swelling bentonite has excellent dry properties and is used for bonding foundry sand and iron-ore pellets. Most of the nonswelling bentonite has very good green-bond properties and is used in foundries employing the green-mold technique. Bentonite is also used in petroleum refining as a catalyst, and fuller's earth is sold for clarifying and processing mineral and vegetable oils. Some bentonite or fuller's earth is treated or "activated" with acid to improve its effectiveness in processing oil, and the activated clay is usually referred to as bleaching clay. A fuller's earth product termed "absorbent granules" is used for many purposes, such as an agent for absorbing oil, grease, and chemicals from floors, as an animal litter, and as a soil conditioner. Both fuller's earth and bentonite are used as carriers for insecticides and fungicides, and minor quantities of bentonite are sold for many other uses, such as sealing irrigation canals and reservoirs.

The first shipment of bentonite for commercial purposes was made in 1888 from Rock Creek, Wyo., by William Taylor. Fuller's earth was first produced in the United States in 1891, when a bed of Tertiary clayey marl near Alexander, Ark., was mined. This clay, however, was used for only a very short time because it proved to be unsatisfactory. In 1893, fuller's earth was discovered through curiosity near Quincy, Fla., when an effort to burn brick proved unsuccessful. The production of both bentonite and fuller's earth has increased more or less steadily since the late 19th century. In 1969 the production of bentonite reached 2.6 million short tons valued at $25.9 million, and the production of fuller's earth reached 984,000 short tons valued at $25.3 million. Wyoming, Mississippi, and Texas are the major bentonite-producing States, and Florida,

Georgia, and Mississippi are the major fuller's earth-producing States. Bentonite production data (fig. 14) are available for only 40 years because before 1930 they were included in the miscellaneous-clay category. The production data for fuller's earth for the past 50 years are shown in figure 14. The average value per ton of bentonite increased from $5.37 in 1936 to $11.83 in 1960 and then decreased to $9.82 in 1969. Some of this decrease in value during the 1960's was due to the increased demand for low-cost poor-quality bentonite as a bond in pelletizing fine-grained iron ores. The average value per ton of fuller's earth increased from $9.28 in 1933 to $25.77 in 1969. Part of this increase in value took place in the 1960's when animal litter, sold in small quantities, became popular at the supermarkets.

Much of the best grade "Wyoming" or "sodium" bentonite occurs in the Mowry Shale of Cretaceous age in Wyoming and South Dakota. The Clay Spur Bentonite bed, near the top of this formation in a belt surrounding the Black Hills, has been a major source of bentonite, and it still contains large reserves. Other beds in the Mowry Shale and younger formations have been mined in the vicinity of the Bighorn Mountains, Wyo. and at scattered localities in Montana. The "calcium" or "southern" bentonite of Cretaceous age is mined in Mississippi and Alabama. Extensive beds of "calcium" bentonite of Tertiary age have been the major sources of bentonite in Texas, Arizona, and California, and smaller deposits of "calcium" bentonite occur in all Western States. A unique magnesium and lithium-bearing high-swelling bentonite termed "hectorite" occurs near Hector, Calif., and at a locality in Arizona. Altered volcanic rock, consisting mainly of montmorillonite, is mined at a locality in Utah and sold as bentonite. Probably similar rock in other States is used as bentonite.

Most fuller's earth deposits occur as beds in sedimentary rock, but some are hydrothermally altered volcanics. The deposits in southern Georgia and northern Florida that consist mainly of palygorskite and montmorillonite are in the Hawthorn Formation of Miocene age. Fuller's earth also occurs in this formation in central peninsular Florida and in the vicinity of Tampa, Fla. Significant tonnages of fuller's earth products are produced from the Twiggs Clay of Eocene age in middle Georgia. The Porters Creek Clay of Paleocene age, which contains enormous tonnages of fuller's earth, is mined at six localities. This formation extends from southeastern Missouri to southern Illinois, across the western part of Kentucky and Tennessee, across northeastern Mississippi, and well into Alabama. The clay in both the Twiggs Clay and the Porters Creek Clay consists chiefly of montmorillonite and poorly crystalline silica in the form of opal or cristobalite. Bentonite is mined at a few places in Texas, California, and elsewhere and is sold as fuller's earth. Altered volcanic rock consisting chiefly of montmorillonite is also mined in Utah and California and is sold as fuller's earth.

Resources of all grades of both bentonite and fuller's earth are very large. The reserves of bentonite must be considered as at least 1 billion tons, and any estimate of presumed resources would be much greater than this figure. The estimate of 1 billion tons includes large deposits of bentonite suitable for bonding iron-ore pellets, but it is classed as submarginal for uses such as drilling mud. The reserves of very high grade colloidal bentonite are limited, and deposits of this type are in demand. Resources of fuller's earth are tentatively estimated at 2 billion tons. Almost any figure, however, could be used here, if all the material equivalent to the grade of fuller's earth used in the past, but now considered submarginal is included. This would include much of the extensive Porters Creek Clay, the Twiggs Clay, thick opal claystone beds, and many scattered impure or low-grade bentonites.

MISCELLANEOUS CLAY

The term "miscellaneous clay" is used by the U.S. Bureau of Mines for clays and shales that do not fit any of the other five categories. The miscellaneous clay and shale may be any color and may contain a large amount of impurities, but the color and impurities may give the clay the necessary properties to make the final product a salable item. Miscellaneous clays and shales are used chiefly in making fired products, but some are used in the unfired form. The unfired uses are as follows: Shale for filler in paint and asphalt; clay for abrasives, termed "rottenstone"; shale for "clay dummies" used to pack dynamite in blasting holes; and clay used for plugging oil and gas wells. These products are easily processed, requiring only drying, grinding, and bagging. Fired products made from miscellaneous clay and shale include face and structural brick, vitrified sewer pipe, drain tile, flue tile, conduits, pottery, and stoneware and floor, wall, and roofing tile. In addition to these uses, clay and shale are used in the manufacture of portland cement and lightweight aggregate.

The demand for miscellaneous clay has increased

in the United States so that in 1969, 42.3 million short tons, valued at $63.3 million, of miscellaneous clay and shale was produced. Every State, except Alaska and Rhode Island, has produced miscellaneous clay products. The States producing over 1 million tons in 1969 were Alabama, California, Georgia, Illinois, Indiana, Iowa, Kentucky, Maryland, Michigan, Mississippi, Missouri, New York, North Carolina, Ohio, Pennsylvania, South Carolina, Tennessee, Texas, and Virginia. Miscellaneous clay production increased tremendously in the 1944–46 period (fig. 14) because there was an increase in building construction following World War II. Before that time, clay production fluctuated considerably, but since then production has been steady. The average value per ton of miscellaneous clay was lowest at $0.72 in 1944 and highest at $2.91 in 1929, just before the depression. The average value per ton in 1969 was $1.49.

Miscellaneous clay and shale occur in rocks ranging in age from Precambrian to Holocene and are formed by several different geologic processes. Rocks used for miscellaneous clay products include both fresh and weathered shale, weathered and fresh schist, slope wash and alluvium, loess, and ferruginous saprolite. Underclay beds and kaolin are also used in heavy-clay products, and some production of these clays is reported as miscellaneous clay by the U.S. Bureau of Mines.

Reserves of miscellaneous clay and shale are enormous in many areas of the United States, but a few plants in or near metropolitan areas have raw-material-supply and air-pollution problems. The suburban spread of large cities, especially on the east coast, has engulfed a few brick and tile plants and their clay and shale resources. Some plants must be relocated or face increasing costs of transporting raw material, and other plants will have to install smoke and dust clarifiers. Future demands for products made from miscellaneous clay and shale can be expected to increase at the same rate as demands for the past two decades (fig. 14). The demand for structural clay products should continue to grow, although competition from other building materials will also continue to increase. The demand for shale in making lightweight aggregate continues to increase and may replace much of the sand and gravel which are being depleted near some of the large eastern cities.

Resources of miscellaneous clay and shale are virtually inexhaustible. The average value per ton is so low that the economics of land values, mining costs, production problems, transportation, market demands, and competition are much more important.

SUMMARY OF RESOURCES

A summary of the resources of the various types of clays is given in table 25.

TABLE 25.—*Summary of clay resources of the United States*

Type of clay	*Reserves* [1] *(tons)*	*Potential resources* [2] *(tons)*	*Remarks*
Kaolin	>300 million		Chiefly in Georgia, Alabama, and Mississippi.
Do		5 billion	Lower grade than reserves.
Ball clay	4 million		Chiefly in Kentucky, Tennessee, and Mississippi.
Do		50 million	Lower grade than reserves.
Fire clay	1 billion		Refractories (low to medium duty).
Do	500 million		Refractories (high duty); flint and nodular flint clays.
Do		7 billion	
Bentonite	1 billion	>1 billion	All grades. Limited reserves of high-grade colloidal type. Chiefly in Wyoming, South Dakota, Mississippi, and Alabama.
Fuller's earth		2 billion	Chiefly in Georgia, Florida, Alabama, Kentucky, Tennessee, Mississippi, Missouri, Illinois, Texas, and California. Total probably greater.
Miscellaneous clays.	Enormous	Virtually inexhaustible.	

[1] Reserves: Identified deposits from which minerals can be extracted profitably with existing technology and under present economic conditions.
[2] Potential resources: Identified mineral deposits not profitably recoverable with existing technology and economic conditions and undiscovered mineral deposits whether of recoverable or subeconomic grade.

ENVIRONMENTAL CONSIDERATIONS

Almost all clay deposits are mined from open pits; heavy equipment is used to remove the overburden and dig the clay. Surface mining destroys the beauty of the countryside and may pollute streams and rivers. Most States require clay producers to install settling ponds to prevent contaminiation of the streams; some States require open pits to be backfilled and covered with vegetation to restore the mined-out areas. Many older abandoned pits are, however, ugly scars detracting from the beauty of the countryside. Many clay-processing plants have installed, and others will be required to install, smoke- and dust-control systems to prevent atmospheric pollution. This, along with increased mining costs, will raise the future market prices of manufactured clay products.

PROBLEMS FOR RESEARCH

More geologic studies are needed related to clay deposits, especially bentonite and fuller's earth, and

increased awareness is needed by the geologic profession of the value of clay deposits. The economic information needed on clay occurrences in areas currently being mapped are mineralogy, purity, thickness, areal distribution, overburden, and potential uses. Many geologic reports of areas containing clay deposits either have ignored those deposits or have given them cursory attention. To help in evaluating potential uses, clay-testing laboratories should be made available to the Federal and State geological surveys and to the public.

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COAL

By Paul Averitt

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ABSTRACT OF CONCLUSIONS

The estimated coal resources of the United States remaining in the ground as of January 1, 1972, totaled 3,224 billion tons. Of this large total, 1,581 billion tons, or 49 percent, is classed as identified, and 1,643 billion tons, or 51 percent, is classed as hypothetical.

Stripping coal resources remaining in the ground as of January 1, 1968, totaled 118 billion tons, or about 7.5 percent of the identified resources.

World coal resources are estimated to total 16,830 billion tons, of which 9,500 billion tons is classed as identified, and 7,330 billion tons is classed as hypothetical. The United States contains about one-fifth of estimated total world resources.

On a uniform Btu basis, U.S. coal resources are larger than the combined domestic resources of petroleum, natural gas, oil shale, and bituminous sandstone. The prolonged future need for energy in ever-increasing quantities, and the prospect of decreasing availability of and increased prices for petroleum and natural gas, have focused very sharp attention on coal as an alternative source of synthetic gas, liquid fuels, and lubricants.

INTRODUCTION

Coal is widespread and abundant in the United States. Coal-bearing rocks underlie about 13 percent of the land area of the 50 States, and are present in varying amounts in parts of 37 States (Trumbull, 1960; Barnes, 1961). The ready availability of coal has contributed substantially to the growth and industrial development of the nation.

On any basis of analysis, U.S. resources of coal are larger than the combined resources of petroleum, natural gas, oil shale, and bituminous sandstone, but use of coal lags behind use of both petroleum and natural gas because these two fuels are cleaner to burn and easier to handle. In spite of this handicap, annual coal production in the United States ranges typically from 500 to 600 million tons. About 10 percent of the annual production is exported, primarily to Japan, Canada, and western Europe.

Of coal consumed annually in the United States, about 62 percent is used in the production of elec-

tric power, 20 percent is used by the steel industry, 16 percent by the manufacturing industry, and 2 percent for all other purposes. Coal is also of great future value and importance as a subsidiary source of synthetic gas, liquid fuels, and lubricants.

ENVIRONMENT OF COAL ACCUMULATION

Coal is the compressed and altered residue of plants that grew in ancient fresh- or brackish-water swamps. As the plant remains accumulated they were transformed into peat; later they were altered by diagenesis (chemical and physical changes occurring before they became solidified), and still later by metamorphism (chemical and physical changes brought about by pressure and heat after they became solidified). Coal contains widely varying amounts of sand, silt, and mud that was washed into the peat swamps, and this admixed sediment forms the bulk of the ash of burned coal. The physical and chemical properties of coal and the coalification process have been described in considerable detail by Schopf (1948; 1956) and by Dapples and Hopkins (1969).

The accumulation of peat requires a humid climate to support a rich growth of vegetation, and a high water table to permit prolonged accumulation of plant material in a reducing environment (See "Peat," this volume). Most of the large peat deposits of Pennsylvanian age that were the precursors of coal mined extensively in the Eastern and Central United States were formed near sea level—some in estuaries or coastal lagoons, others on large deltas or many coalescing deltas, others on low-lying, broad coastal plains. These features form characteristically in areas of gentle downwarping of the sea floor marginal to the edges of an eroding landmass. This topographically low position in an area of gentle downwarping permitted periodic transgressions of the sea. Some thick coal beds of very wide areal extent required a very large and wide coastal plain, a prolonged optimum rate of plant growth and accumulation, a slow rate of subsidence, and an equally slow encroachment of the sea over periods measured in centuries.

The transgressive sea ultimately covered the peat-forming swamp and terminated plant growth. The eroding landmass continued to supply sand, silt, and mud to the sea, and this material settled in layers over the submerged peat swamp. In time, depending in length on the rate of sedimentation, the depth of the transgressive sea, and the rate of subsidence, this sedimentary material built up new deltas, lagoons, and coastal plains conducive to the development of new, younger peat-forming swamps.

This sequence of deposition was repeated many times by intermittent downwarping alone, but the sequence might have been prolonged, shortened, or terminated at any time by relatively minor movements of land relative to the sea floor. In the very delicate balance between sedimentation, subsidence, and uplift of the land, the sea also regressed from time to time. Peat swamps obviously formed during the regressive phase of the cycle, but these were subject to oxidation and are less commonly preserved. These cyclic repetitions of the conditions allowing the formation of coal are documented in many of the world's coal fields, but rarely as strikingly as in a sequence of several thousands of feet of sedimentary rock in West Virginia that contains 117 coal beds of sufficient geologic and economic interest to have been described and named.

Weight of the overlying sedimentary rock, heat produced by depth of burial, structural deformation, and time all contribute to the progressive compaction and devolatilization of peat to form the higher ranks of coal, which are discussed below. A subsequent major uplift of the land relative to the sea has raised the U.S. coal fields to their present positions, exposing them to erosion and to view, thereby permitting study and mine development.

RANK OF COAL

Coal is classified by rank according to the percentage of fixed carbon and heat content, calculated on a mineral-matter-free basis. As shown in figure 15, the percentage of fixed carbon and the heat content increase from lignite to low-volatile bituminous coal as the percentages of volatile matter and moisture decrease. These changes are primarily the result of depth and heat of burial, compaction, time, and structural deformation. Rank is thus a way of expressing the progressive metamorphism of coal. It is quite independent of grade, which is a way of expressing quality.

As coals of different rank are adapted to different uses, rank is a major basis of differentiation in coal-resource calculations. In accompanying tables and figures, the coal resources are expressed in short tons. If arithmetic adjustments were made for the contained heat values, the distribution patterns would be changed somewhat because of the lower heat values of lignite and subbituminous coal.

GRADE OF COAL

Coal is classified by grade largely according to the content of ash, sulfur, and other deleterious constituents. Thus far in work on coal resources, a preliminary classification on the basis of sulfur

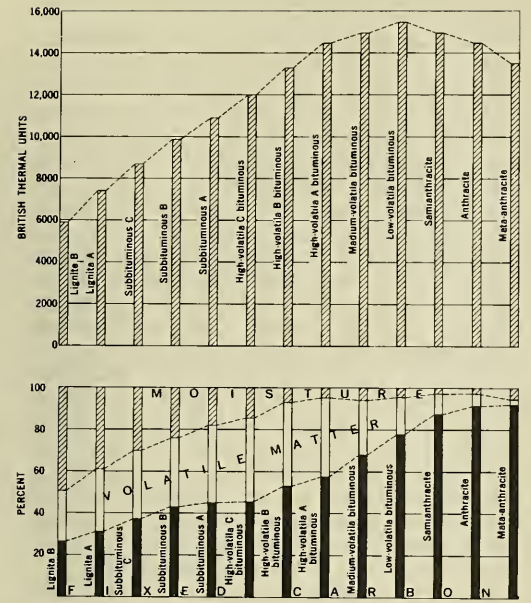

FIGURE 15.—Comparison on moist, mineral-matter-free basis of heat values and proximate analyses of coal of different ranks.

content has been made, but classification on the basis of ash content has not been made, because ash is a more highly variable component than sulfur. In recent years, information on trace elements in coal has increased somewhat, but classification according to trace-element content is not yet possible.

SULFUR

Sulfur is an undesirable element in coal. It lowers the quality of coke and of the resulting iron and steel products. It contributes to corrosion, to the formation of boiler deposits, and to air pollution. Its presence in spoil banks inhibits the growth of vegetation. As sulfuric acid, it is the main deleterious compound in acid mine waters, which contribute to stream pollution.

The sulfur content of coal in the United States ranges from 0.2 to about 7.0 percent, but the average in all coal is 1.0–2.0 percent. Most of the sulfur, perhaps 40–80 percent, occurs as a constituent of pyrite and marcasite (FeS_2). The remainder occurs as hydrous ferrous sulfate ($FeS_4 \cdot 7H_2O$), derived by weathering of pyrite, as gypsum ($CaSO_4 \cdot 2H_2O$), and as organic sulfur in combination with the coal-forming vegetal material (Walker and Hartner, 1966).

The percentage of sulfur and of pyritic sulfur is highest in bituminous coals of Pennsylvanian age in the Appalachian and Interior coal basins. The percentage is relatively low, generally less than 1 percent, in subbituminous coal and lignite of the Rocky Mountain and Northern Great Plains regions. This relation is shown clearly in table 26.

TABLE 26.—*Distribution, in percent, of identified[1] United States coal resources according to rank and sulfur content[2]*

Rank	Sulfur content (in percent)		
	Low 0–1	Medium 1.1–3.0	High 3+
Anthracite	97.1	2.9	---
Bituminous coal	29.8	26.8	43.4
Subbituminous coal	99.6	.4	---
Lignite	90.7	9.3	---
All ranks	65.0	15.0	20.0

[1]Identified resources: Specific, identified mineral deposits that may or may not be evaluated as to extent and grade, and whose contained minerals may or may not be profitably recoverable with existing technology and economic conditions.

[2] From DeCarlo, Sheridan, and Murphy (1966).

The conspicuously large percentage of low-sulfur coal in the United States, shown on the last line of table 26, is primarily due to the fact that the resources of low-sulfur subbituminous coal and lignite concentrated in the Rocky Mountain and Northern Great Plains regions represent about 54 percent of total identified resources.

RESEARCH ON REMOVAL OF SULFUR

Pyrite and marcasite have a high specific gravity, and most of this material can be removed from coal by various washing and cleaning procedures. The other forms of sulfur have lower specific gravities and are more intimately mixed with the coal, and consequently are less easily removed. Between 60 and 65 percent of all coal mined in the United States is cleaned to remove pyritic and inert material before use. However, in spite of such large-scale cleaning, the average sulfur content of all coal used in the United States is still nearly 2 percent.

Current efforts to reduce the sulfur content of coal and of flue gas take many forms:

1. Much research is in progress on methods to remove SO_2 and SO_3 from flue gas. This can be done by several well-known chemical processes, and the technical problems inherent in the large-scale commercial application of chemical processes are likely to be solved in the near future.
2. Meanwhile, the search for low-sulfur coal has

been intensified, particularly in the Eastern States, and the use of lower-sulfur coal has been increased. A few older coal-burning utility plants in the Midwest have converted from high-sulfur local coal to low-sulfur Rocky Mountain coal. This substitution has required payment of transportation costs of $3–$5 per ton, and acceptance of the lower heat content of Rocky Mountain coal. Such high transportation costs obviously will intensify research efforts mentioned in item 1.

3. Much research is in progress on methods to produce a high-Btu, sulfur-free gas from coal. This is also a technical possibility soon to be realized. It has the multiple advantages of lowering the costs of long-distance transportation of energy, of eliminating the sulfur problem, of augmenting declining resources of natural gas, of reducing dependence on foreign sources of oil and gas, and ultimately permitting use of high-sulfur eastern coal.
4. Research on improved methods of producing electric power by nuclear fission and fusion is continuing.

These varied avenues of approach suggest that the amount of sulfur released to the atmosphere by the burning of coal will soon be greatly reduced.

MINOR ELEMENTS IN COAL

Coal contains small quantities of virtually all metallic and nonmetallic elements, that were introduced into the coal bed in one or all of four different ways:

1. As inert material washed into the coal swamp at the time of plant accumulation.
2. As a biochemical precipitate from the swamp water.
3. As a minor constituent of the original plant cells.
4. As a later addition, introduced after coal formation, primarily by ground water moving downward and laterally.

When coal is burned, most of these elements are concentrated in the coal ash, but a few of the more volatile elements are emitted into the atmosphere. Coal ash is composed largely of the oxides of Si, Al, Fe, Ca, Mg, K, Na, and S, which typically make up 93–98 percent of the total weight of the ash (Abernethy and others, 1969a). The remaining few percent of coal ash is made up of small individual amounts of many other elements, which differ in variety and quantity in different areas and beds. These elements are generally measured in parts per million or billion, and for this reason are termed minor elements, although they may not be minor elements in other contexts.

The minor elements in coal are of considerable interest because some may become of future resource importance, and others may be pollutants. Most of the minor elements occur in coal in about the same concentration as their estimated concentration in the earth's crust, but 25–30 elements occur locally in greater concentration and these have received the most study. A few elements, notably U, Ge, As, B, and Be, occur locally in vastly greater concentrations than their estimated concentration in the earth's crust; others, including Ba, Bi, Co, Cu, Ga, La, Pb, L, Hg, Mo, Ni, Sc, Se, Ag, Sr, Sn, V, Y, Zn, and Zr, occur locally in appreciably greater concentrations. Other elements of interest that generally occur in lower concentrations than those listed above include Cr, Mn, P, Te, Tl, Ti, and W. It should be noted that the concentration of an element in excess of the estimated concentration in the earth's crust, although of great interest and geologic significance, does not necessarily imply an economic or paramarginal concentration, because that is determined by the concentration in typical commercial sources of the respective element.

Reports by Abernethy and Gibson (1963); Abernethy, Peterson, and Gibson (1969a, b); Zubovic (1966a, b); Zubovic, Sheffey, and Stadnichenko (1967); Zubovic, Stadnichenko, and Sheffey (1960a, b, c; 1961a, b; 1964; and 1966); and by Sun, Vasquez-Rosas, and Augenstein (1971) summarize available information concerning minor elements in coal. A selected bibliography on trace elements in coal, applicable primarily to U.S. coals, has been compiled by Averitt, Breger, Gluskoter, Swanson, and Zubovic (1972).

UNITED STATES COAL RESOURCES

The remaining coal resources of the United States as of January 1, 1972, are estimated to total 3,224 billion tons. Of this large total, 1,581 billion tons, or 49 percent, has been identified on the basis of mapping and exploration, and the remainder of 1,643 billion tons, or 51 percent, is classed as hypothetical because it has been determined by extrapolation of the data on identified resources into unmapped and unexplored areas. The distribution of this tonnage by State is given in table 27.

The figures in table 27, and in subsequent tables and figures, express resources in the ground. The recoverability in coal mining ranges from 40 to 90 percent, depending largely on the method of mining, but it is influenced by many other diverse factors such as the nature of the roof rock, joints, faults,

TABLE 27.—*Total estimated remaining coal resources of the United States, January 1, 1972*

[In millions of short tons. Figures are for resources in the ground, about half of which may be considered recoverable. Includes beds of bituminous coal and anthracite 14 in. or more thick and beds of subbituminous coal and lignite 2½ ft or more thick]

State	Identified resources [1]						Hypothetical resources [2]			Total resources
	Overburden 0–3,000 ft						Overburden 0–3,000 ft	Overburden 3,000–6,000 ft	Overburden 0–6,000 ft	Overburden 0–6,000 ft
	Estimated identified resources remaining in the ground, Jan. 1, 1972						Estimated hypothetical resources in unmapped and unexplored areas reasonably near the surface [3]	Estimated hypothetical resources in deeper structural basins [3]	Total estimated hypothetical resources	Total estimated identified and hypothetical resources remaining in the ground Jan. 1, 1972
	Bituminous coal	Subbituminous coal	Lignite	Anthracite and semianthracite	Total	Source of estimate				
Alabama	13,342	0	2,000	0	15,342	Culbertson (1964); T. A. Simpson (written commun., 1972).	20,000	6,000	26,000	41,342
Alaska	19,413	110,668	[4]	[5]	130,081	Barnes (1961; 1967)	130,000	6,000	135,000	265,081
Arizona	[6] 21,246	[6]	0	0	21,246	Peirce and others (1970)[7].	0	0	0	21,246
Arkansas	1,638	0	350	430	2,418	Haley (1960)	4,000	0	4,000	6,418
Colorado	62,339	18,242	0	78	80,659	Landis (1959)	146,000	145,000	291,000	371,659
Georgia	24	0	0	0	24	Johnson (1946)[7]	60	0	60	84
Illinois	139,124	0	0	0	139,124	Simon (1966)[7]	100,000	0	100,000	239,124
Indiana	34,573	0	0	0	34,573	Spencer (1953)	22,000	0	22,000	56,573
Iowa	6,509	0	0	0	6,509	Landis (1966)	14,000	0	14,000	20,509
Kansas	18,674	0	[8]	0	18,674	Schoewe (1962; 1968)[7]	4,000	0	4,000	22,674
Kentucky	64,842	0	0	0	64,842	Huddle and others (1963).	52,000	0	52,000	116,842
Maryland	1,158	0	0	0	1,158	Averitt (1969)	400	0	400	1,558
Michigan	205	0	0	0	205	Cohee and others (1950).	500	0	500	705
Missouri	31,014	0	0	0	31,014	Robertson (1971)[7]	18,200	0	18,200	49,214
Montana	2,299	131,855	87,521	0	221,675	Combo and others (1949; 1950)[7].	157,000	0	157,000	378,676
New Mexico	10,752	50,671	0	4	61,427	Read and others (1950)	27,000	21,000	48,000	109,427
North Carolina	110	0	0	0	110	Reinemund (1949; 1956).	20	5	25	135
North Dakota	0	0	360,630	0	360,630	Brant (1953)	180,000	0	180,000	530,630
Ohio	41,358	0	0	0	41,358	Brant and DeLong (1960).	2,000	0	2,000	43,358
Oklahoma	3,281	0	[8]	0	3,281	Trumbull (1957)	20,000	10,000	30,000	33,281
Oregon	50	284	0	0	334	R. S. Mason (written commun., 1965)[7].	100	0	100	434
Pennsylvania	66,759	0	0	20,510	77,269	Reese and Sisler (1928); Arndt and others (1968)[7].	[9] 10,000	0	10,000	87,269
Rhode Island	0	0	0	[10]	----	Toenges and others (1948).	0	0	0	----
South Dakota	0	0	2,031	0	2,031	D. M. Brown (1962)	1,000	0	1,000	3,031
Tennessee	2,572	0	0	0	2,672	Luther (1959; written commun., 1966).	2,000	0	2,000	4,672
Texas	6,048	0	6,824	0	12,872	Mapel (1967); Perkins and Lonsdale (1965).	14,000	0	14,000	26,872
Utah	[11] 23,541	[11] 180	0	0	[11] 23,721	Doelling 1970, 1971a, b, c, d, e, f, Doelling and Graham, (1970; 1971); H. H. Doelling (written commun., 1971).	[12] 21,000	36,000	56,000	79,721
Virginia	9,352	0	0	335	9,687	Brown and others (1962).	5,000	100	5,100	14,787
Washington	1,867	4,190	117	5	6,179	Beikman and others (1961).	30,000	15,000	45,000	51,179
West Virginia	100,628	0	0	0	100,628	Headlee and Nolting (1940).	0	0	0	100,628
Wyoming	12,705	107,951	[2]	0	120,656	Berryhill and others (1950; 1951).	326,000	100,000	425,000	545,656
Other States	[13] 610	[14] 32	[15] 46	0	688	----------	1,000	0	1,000	1,688
Total	686,033	424,073	449,519	21,362	1,580,987		1,306,280	337,105	1,643,385	3,224,372

[1] Identified resources: Specific, identified mineral deposits that may or may not be evaluated as to extent and grade, and whose contained minerals may or may not be profitably recoverable with existing, technology and economic conditions.

[2] Hypothetical resources: Undiscovered mineral deposits, whether of recoverable or subeconomic grade, that are geologically predictable as existing in known district.

[3] Estimates by H. M. Beikman (Washington), H. L. Berryhill, Jr. (Wyoming), R. A. Brant (Ohio and North Dakota), W. C. Culbertson (Alabama), H. H. Doelling (Utah), K J. Englund (Kentucky and Virginia), B. R. Haley (Arkansas), E. R. Landis (Colorado and Iowa), E. T. Luther (Tennessee), R. S. Mason (Oregon), C. E Robinson (Missouri), J. A. Simon (Illinois), J. V. A. Trumbull (Oklahoma), C. E. Wier (Indiana), and the author for the remaining States.

[4] Small resources of lignite included under subbituminous coal.

[5] Small resources of anthracite in the Bering River field believed to be too badly crushed and faulted to be economically recoverable (Barnes, 1961).

[6] Includes coal in the Dakota Formation of the Black Mesa field, some of which may be of subbituminous rank. Does not include small resources of thin and impure coal in the Deer Creek and Pinedale fields.

[7] See other summary reports on coal resources in individual States as follows: Arizona (Averitt and O'Sullivan, 1969); Georgia (Butts and Gildersleeve, 1948; Sullivan, 1942); Illinois (Cady, 1952); Kansas (Abernathy and others, 1947); Missouri (Hinds, 1913; Searight, 1967); eastern Montana (Averitt, 1966); Ohio (Struble and others, 1971); Oregon (Mason and Erwin, 1965; Mason, 1969); Pennsylvania anthracite (Ashley, 1945; Ashmead, 1926; Rothrock, 1950); and Utah (Averitt, 1964).

[8] Small resources of lignite in beds generally less than 30 in thick.

[9] From Ashley (1944).

[10] Small resources of mete-anthracite in the Narragansett basin believed to be too graphitic and too badly crushed and faulted to be economically recoverable as fuel

[11] Excludes coal in beds less than 4 ft thick.

[12] Includes coal in beds 14 in. or more thick, of which 14,000 million tons is in beds 4 ft or more thick.

[13] California, Idaho, Nebraska, and Nevada.

[14] California and Idaho.

[15] California, Idaho, Louisiana, and Mississippi.

and the need to protect oil and gas wells and fields. From the long-term national point of view, average recoverability is probably about 50 percent. However, it is not desirable to report coal resource data on an arbitrary recoverable basis, because experience with most commodities has shown very significant long-term changes in what is regarded as economically recoverable. Coal in the ground is a more certain value that can be modified now or in the future by any recoverability factor deemed appropriate.

IDENTIFIED RESOURCES

DISTRIBUTION BY SELECTED CATEGORIES

In addition to the distribution by rank of the identified resources of 1,581 billion tons as presented in table 27, about 60 percent of this total has been classified into additional categories according to the thickness of overburden, degree of reliability of estimates, and thickness of beds as shown in figure 16. This classified tonnage is fairly large and is widely distributed in 21 States; it is likely to be reasonably representative of the total identified tonnage.

Overburden.—Figure 16 clearly shows the pronounced concentration of identified resources in the 0–1,000-foot overburden category. This concentration results in part from the fact that coal-bearing rocks are near the surface in most parts of the United States, and in part from the fact that progressively less information is available for the more deeply buried beds. Much of the tonnage classed as hypothetical in figure 17 is in the 1,000–2,000-foot and the 2,000–3,000-foot overburden categories. As exploration and development are carried to greater depth it is certain that the identified resources will be considerably increased by addition of tonnage in the deeper overburden categories.

Degree of reliability of estimates.—Figure 16 also shows the progressive increase in tonnage from the measured to the inferred categories. In the 0–1,000-foot overburden category, for example, 8 percent of the tonnage is classified as measured, 23 percent as indicated, and 58 percent as inferred. The same relation can be observed in the deeper overburden categories. The large percentage of inferred coal reflects merely distance from points of known information. Resources classified as "inferred" obviously exist, but the locations of such tonnage may differ slightly from those assumed to make the calculations. As mapping and exploration continue, the

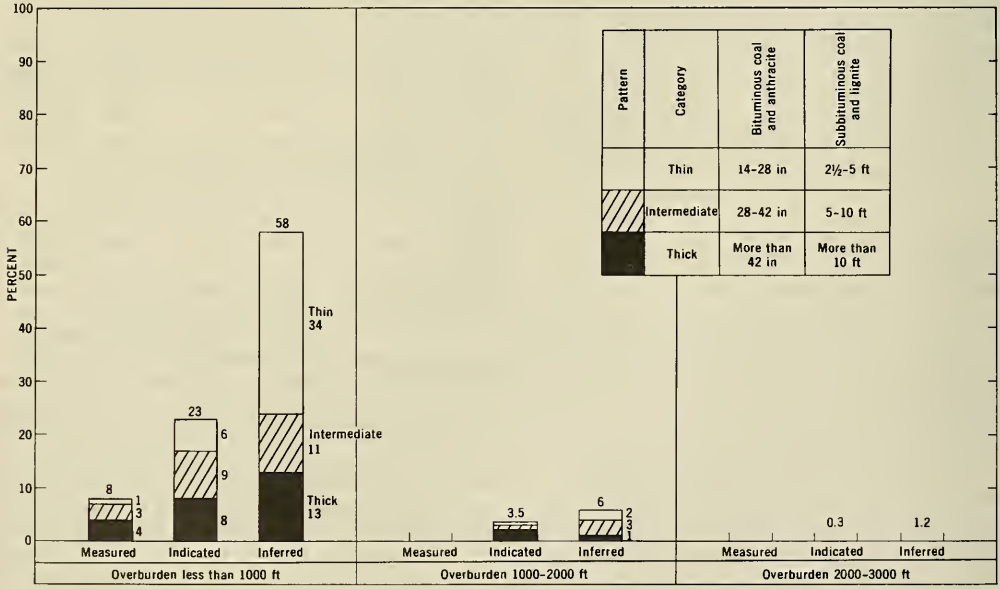

FIGURE 16.—Approximate percentage distribution of original identified U.S. coal resources by major resource categories.

percentage of coal classified as measured and indicated will surely increase.

Thickness of beds.—Coal in thick beds, 0–1,000 feet below the surface comprises 4 percent measured, 8 percent indicated, and 13 percent inferred, for a total of 25 percent of the identified resources shown in figure 16. This percentage, when applied to the total of 1,581 billion tons, is equivalent to nearly 400 billion tons. This choice tonnage is in a thickness and overburden category comparable to that of coal now being mined, and is therefore of current and near-current economic interest.

Coal in beds of intermediate thickness, 0–1,000 feet below the surface, makes up 23 percent of the identified resources, and is equivalent to 350 billion tons. This tonnage is of less immediate economic interest than tonnage in the thicker beds. However, some coal in this thickness and overburden category is currently being mined, and the total must be considered a paramarginal resource that will become of increasing economic interest and importance in the future.

Coal in thin beds, 0–1,000 feet below the surface, makes up 41 percent of the identified resources, and coal in all thickness categories, 1,000–3,000 feet below the surface, makes up the remaining 11 percent. This coal is of little current economic interest.

The amount in any category or combination of categories can be derived from figure 16 by the procedure used above.

STRIPPING COAL RESOURCES

In a recently published study, the U.S. Bureau of Mines (1971) concluded that the remaining stripping coal resources of the United States as of January 1, 1968, totaled 118 billion tons. Of this total, about 90 billion tons, or 80 percent, is within reach by present machinery and methods of mining, but only 45 billion tons is both available for use and economically recoverable.

For purpose of comparison, the larger total of 118 billion tons of stripping coal resources is 7.5 percent of the total of 1,581 billion tons of remaining identified resources as reported in table 27.

The 45 billion tons of potentially recoverable stripping coal includes 32 billion tons of low-sulfur coal (less than 1 percent), 4 billion tons of medium-sulfur coal (1–2 percent), and 9 billion tons of high-sulfur coal (more than 2 percent).

HYPOTHETICAL RESOURCES

The preceding analysis of the distribution of identified coal resources provides convincing evidence that unmapped and unexplored areas in known coal fields contain substantial additional resources that must be classed as hypothetical. The approximate magnitude of the additional hypothetical resources has been estimated by a process of extrapolation from nearby areas of identified resources, and estimates for each State are presented in separate columns in table 27. The total tonnage of hypothetical resources actually exceeds by a small amount the tonnage of identified resources. Figure 17 shows the percentage relation between identified and hypothetical resources in four overburden categories.

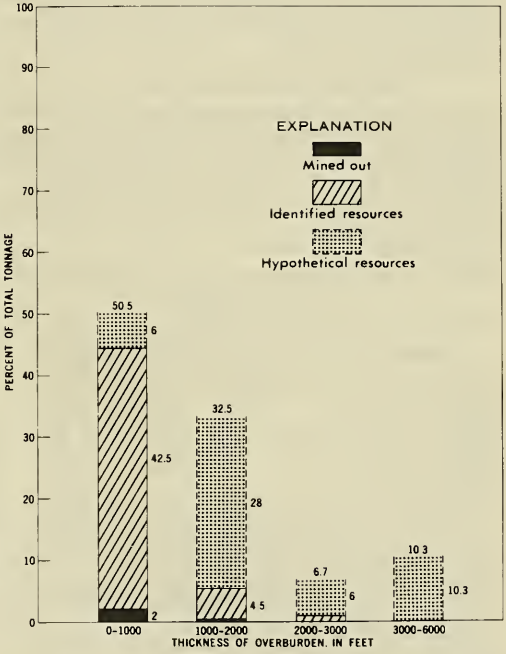

FIGURE 17.—Probable distribution of total estimated U.S. coal resources according to thickness of overburden.

Although large, the hypothetical resources are, for the most part, relatively inaccessible for mining at present, and a more exact delineation of the magnitude, distribution, and future utility of such resources will require a substantial amount of detailed geologic mapping, exploration, and study over a long period. Nevertheless, the estimated hypothetical resources constitute an important part of the total resource that needs to be considered in

future planning for the utilization of all energy resources.

SPECULATIVE RESOURCES

The resources presented in table 27 and discussed under the headings of identified and hypothetical resources represent total resources within limits established by the minimum thickness of coal beds and the maximum thickness of overburden. The major geologic features of the United States are known well enough to justify the statement that, in all probability, no major coal fields remain to be discovered. Hence the coal resources of the United States are all either identified or hypothetical. Because there are no undiscovered districts, there are no speculative resources.

WORLD COAL RESOURCES

The original identified coal resources of the world total about 9,500 billion tons, the additional hypothetical resources total about 7,330 billion tons, and the two categories combined total 16,830 billion tons. The distribution of this tonnage by continents is shown in table 28.

TABLE 28.—*Estimated total original coal resources of the world, by continents* [1]

[In billions of short tons]

Continent	Identified resources [2]	Hypothetical resources [3]	Estimated total resources
Asia [4]	[5] 7,000	4,000	[6] 11,000
North America	1,720	2,880	4,600
Europe	620	210	830
Africa	80	160	240
Oceania	60	70	130
South and Central America	20	10	30
Total	[5] 9,500	7,330	[6] 16,830

[1] Original resources in the ground in beds 12 in. or more thick and generally less than 4,000 ft below the surface, but includes small amounts between 4,000 and 6,000 ft.

[2] Identified resources: Specific, identified mineral deposits that may or may not be evaluated as to extent and grade, and whose contained minerals may or may not be profitably recoverable with existing technology and economic conditions.

[3] Hypothetical resources: Undiscovered mineral deposits, whether of recoverable or subeconomic grade, that are geologically predictable as existing in known districts.

[4] Includes European U.S.S.R

[5] Includes about 6,500 billion short tons in the U.S.S.R.

[6] Includes about 9,600 billion short tons in the U.S.S.R. (Hodgkins, 1961, p. 6).

The figures for the United States as shown in table 27 are included in the total for North America in table 28. On the basis of identified resources, the United States contains about one-sixth of world resources; on the basis of total resources, the United States contains about one-fifth of world resources.

Table 28 shows clearly that Asia contains most of the world's total coal resources. This tonnage is concentrated in the U.S.S.R. and China, both of which are important coal-producing countries. The table also shows that the coal resources of Europe have been well established by mapping and exploration, and that estimates will not be greatly increased by future work. Finally, table 28 shows that Africa, Oceania, and South America contain small resources as compared with the rest of the world, but that the quantities assumed to be present are sufficient to justify continued exploration and development. (See Averitt, 1969, p. 81–85.)

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COBALT

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ABSTRACT OF CONCLUSIONS

Cobalt is a hard, silvery white metal of strategic importance in the production of high-temperature alloys, permanent magnets, and tool steels. Currently the United States consumes about 15 million pounds of the world's annual cobalt production of 45 million pounds, but the domestic production, only about 3 million pounds, is derived from recycled scrap and the byproduct of iron mining in Pennsylvania. That the amount of cobalt mined annually in the United States is so small is more a function of economic and technological problems than the lack of ore deposits containing cobalt. Nearly all the cobalt that now reaches the world markets is the byproduct of mining sulfide ores of associated metals, chiefly copper, nickel, and iron in central Africa, Canada, and Finland. Large potential supplies of cobalt are in lateritic iron-nickel deposits of tropical regions. More than 1 billion pounds of cobalt is in the identified resources of the United States, chiefly in various types of deposits of sulfide ore in the Appalachian and midcontinent regions. Published data indicate that the identified cobalt resources of the world contain more than 9.9 billion pounds of the element. Additional large amounts of cobalt are in the manganese nodules of the sea floor. The world's hypothetical and speculative resources of cobalt likely amount to many more billions of pounds of metal.

INTRODUCTION

Cobalt (Co) is a hard, moderately malleable and ductile, strongly magnetic, silvery, white metal of great commercial importance in metallurgical applications. The major uses of cobalt in the United States are, in order of consumption: (1) high-temperature alloys, the superalloys, (2) permanent-magnet alloys, (3) cutting and wear-resistant alloys, (4) tool steels, (5) miscellaneous alloys, (6) pigments and driers for paint, ink, lacquer, and varnish, (7) ground-coat frit for enameling, (8) catalysts in the chemical and petroleum industries, (9) ceramic glazes, (10) additives and supplements to sheep and cattle feed, and (11) as radioactive Co^{60} in several medical applications.

In 1969 the United States consumed about 15 million pounds of the world's estimated production of 45 million pounds of cobalt (table 29). Domestic sources provided only about 3 million pounds, derived from recycled scrap and as a moderate-yield byproduct from iron mines in southeastern Pennsylvania (DeHuff, 1971, p. 399). The remaining domestic needs of 12 million pounds were filled by imports from ores originating chiefly in Zaïre, Canada, Morocco, and Zambia.

TABLE 29.—*World production of cobalt in 1969* [1]

[From DeHuff (1971, p. 401). Short tons of contained cobalt; *, estimate]

Country	Production
Australia	*330
Canada	1,602
Cuba	1,700
Finland	1,800
Germany (West)	864
Morocco	*1,700
U.S.S.R.	*1,650
Zaïre	*11,000
Zambia	1,650
Total	22,296

[1] Excluding Bulgaria, East Germany, Poland, and the United States.

The great disparity between domestic production and consumption, particularly during periods of national emergency, is a matter of serious concern. This disparity may well increase in the future. According to Reno (1970, p. 270), the annual demand for cobalt in the United States in the year 2000 is estimated to be at least 18.6 million pounds and possibly as much as 30.5 million pounds. Most of this metal will have to be imported, with the attendant costs in foreign exchange, unless substitutes can be developed or available domestic sources can be utilized more efficiently.

The forecast of cumulative demand for cobalt in the United States from 1968 to the year 2000 ranges from 520 to 670 million pounds (Reno, 1970, p. 273). The world's cumulative demand for cobalt for the same period ranges from 1,645 to 1,997 million pounds. The potential supply of primary cobalt in the world at current prices is more than 8–10 times the cumulative total of domestic demand and more than 2.5 times the cumulative total of world demand. This supply, however, is available only at a rate of 40–50 million pounds per year, chiefly as a byproduct of nickel and copper mining. Supplies are thus tied to production of the major product, but production of these elements will also increase. Under current competitive economic conditions, future supplies will continue to come at no relative increase in current price (Reno, 1970, p. 273) from sulfide deposits in Zaïre, Canada, Morocco, and Zambia, and from the laterites of New Caledonia, Cuba, Indonesia, the Philippines, and other tropical lands. Beginning in 1954, however, the consumption of cobalt in other nations has increased at accelerating rates far in excess of that in the United States (Piedboeuf, 1961, p. 3). The economic competition for available cobalt, especially under emergency conditions, perhaps will become greater in the future.

Alleviation of the increasing demand for the production of cobalt may possibly be found in the discovery and development of acceptable substitutes and the increased recycling of scrap. So far as is known, however, many of the alternate materials proposed as substitutes for cobalt also are strategic industrial metals, including nickel, and for some applications, vanadium, molybdenum, tungsten, and chromium. No substitutes are known, however, for the use of cobalt in carbides and in some tool steels (Reno, 1970, p. 269). In other applications, several organic and mineral catalysts and driers can be used in the place of cobalt, but only at a loss in effectiveness. The same is true of substitutes for Co^{60} as a source of gamma radiation.

Few published data are currently available on the quantities of cobalt-bearing scrap that are recovered and reused in the United States. The quantity may be large, inasmuch as increasing volumes of cobalt-bearing superalloy are being used and the service life of many of the products made from these alloys is relatively short. Permanent magnets are also a potential source of secondary cobalt. According to Reno (1970, p. 268), export statistics show that at least 1.5 million pounds of cobalt-bearing scrap is generated and shipped out of the United States annually.

EXPLOITATION

Cobalt is now produced primarily as a byproduct of the mining and metallurgical processing of copper, nickel, and silver ores. More than half the cobalt produced comes from the strata-bound deposits of copper in central Africa. Major production also comes from sulfide ores of copper, nickel, and iron associated with mafic rocks in Canada and Finland. Currently, only the mines at Bou Azzer, Morocco, are producing cobalt as a major product from vein deposits.

In the United States some cobalt has been produced intermittently for more than 100 years. One of the principal early domestic sources of cobalt production was the Gap nickel mine, Lancaster County, Pa. Joseph Wharton operated the mine until 1893 and smelted the ore containing nickel, copper, and 0.1 percent cobalt, at the Camden Nickel Works. Records indicate that a total of 143,499 pounds of cobalt oxide was produced from 1869 to 1893. Wharton's process for commercially recovering small amounts of cobalt from mixed sulfide ores in the mafic rocks served as a basis for some modern technology used in Canada and Europe. In the lead district of southeast Missouri, the Mine La Motte and Fredericktown areas also have been leading producers of cobalt—at least 5.2 million pounds from 1844 to 1961. The Madison mine, near Fredericktown, produced 2.8 million

pounds of cobalt for the national stockpile of strategic minerals. from 1954 to 1961 (Cornwall and Vhay, 1967, p. 70).

About 400,000–600,000 pounds of cobalt is produced annually from pyrite as a byproduct of mining magnetite at Cornwall, Pa. (Andrews, 1962, p. 161). The mineral production from Cornwall and the Grace mine, near Morgantown, Pa., is now virtually the only primary source of domestic cobalt.

Small amounts of cobalt were produced from the veins of the Blackbird district, Idaho, during World War I, and about 14 million pounds was produced from 1951 to 1959, when the mines closed. The mines were still inactive in 1972. According to Andrews (1962, p. 162), the Magnesia Talc Co., at Burlington, Vt., has produced concentrates containing cobalt and nickel as a product in the froth flotation of talc. Not much information is available, but the concentrates are believed to contain 0.015 percent cobalt and 0.2 percent nickel.

Small production of cobalt has been reported from other places in earlier times—near Chatham, Conn., the Goodsprings and Table Mountain districts, Nevada, and the Quartzburg district, Oregon.

The production of cobalt from laterite ores has been small during the past few decades, but these deposits, which can be mined at relatively low cost by open-pit methods, are destined to become increasingly important. The cobaltiferous laterite, or asbolane, deposits of New Caledonia intermittently have been the leading world producers of cobalt. Although production from this source has been insignificant since 1911, the total cobalt reserves are estimated to be large and readily available for renewed production. In more recent years, chiefly since the beginning of World War II, cobalt has been recovered from laterite ores in Cuba. It is believed that with proper economic incentives this production can be increased substantially. Similar large deposits occur in the Philippines, Indonesia, the U.S.S.R., Western United States, Guatemala, and many other countries.

The history of cobalt production clearly indicates that large ore deposits containing some small amounts of cobalt are widespread in the world, but virtually none are workable for cobalt content alone. The current utilization of the world's cobalt is primarily a matter of economics and technology, and not a question of geologic availability.

Mining, smelting, and other environmental considerations in the production of cobalt are identical with those considered in the chapters of this volume dealing with iron, copper, and nickel.

GEOLOGIC ENVIRONMENT

GEOCHEMISTRY

Cobalt (atomic number, 27; atomic weight, 58.93) is a metallic element whose abundance in the earth's crust is estimated to be about 20 ppm (parts per million). It is a simple element consisting in terrestrial materials almost exclusively of the single stable nuclide Co^{59} except for minor traces of fission-produced and cosmic-ray-produced Co^{60} (Rankama, 1963, p. 393–394). In addition, nine radioisotopes of mass numbers 54–58 inclusive, and 60, 61, 62, and 64, have been made artificially, of which Co^{60} is a highly important source of radioactivity (Rankama, 1963, p. 393). The ionic radius of cobalt in sixfold coordination is 0.72A for Co^{2+} and 0.63A for Co^{3+}, closely similar to the ionic radii of Mg^{2+}, Mn^{4+}, Fe^{2+}, Fe^{3+}, Ni^{2+}, and possibly Zn^{2+}, with all of which it is commonly associated in nature.

The principal concentrations of cobalt are found in mafic and ultramafic igneous rocks. As shown in table 30, the cobalt content progressively decreases

TABLE 30.—*Average cobalt content of igneous rocks*

[Compiled by J. S. Vhay]

Rock type (listed in order of increasing differentiation)	Co (ppm)	Ni (ppm)	Ni/Co
Ultramafic rocks	270	1,900	7
Gabbro	51	133	2.6
Basalt	41	102	2.5
Diabase	31	65	2.3
Intermediate igneous rocks	14	27	1.9
Felsic rocks	5	5.7	1.1

in a differentiation series from ultramafic to acidic rocks. The ratio of nickel to cobalt also decreases during differentiation, chiefly because cobalt enters the lattice of early crystallizing magnesium silicates less readily than nickel, which has an ionic radius closer to magnesium.

The concentrations of cobalt in sedimentary rocks are not well known, in part because of the past difficulty in analysis for the small amounts present in most types of rock. Average figures from a variety of sources indicate about 4 ppm Co in sandstone, 6 ppm in carbonate rocks, and about 40 ppm for shale, clay, mudstone, and siltstone. Few analyses of cobalt in iron-rich sedimentary rocks are available; however, Krauskopf (1955) indicated a range of 20–300 ppm. The cobalt content of phosphorite is reported between 2 and 50 ppm (Krauskopf, 1955). Somewhat higher concentrations are reported in sedimentary deposits that are rich in organic carbon. As much as 500 ppm cobalt has been reported in ashed carbonaceous shale, 148 ppm in ashed coal,

490–3, 280 ppm in ashed petroleum (Krayushkin and others, 1964), and as much as 90,000 ppm, or 9 percent, in ashed asphalt.

During the formation of metamorphic rocks, apparently little movement and concentration of cobalt takes place. Thus, the cobalt content of different metamorphic rocks depends almost entirely on the amount of cobalt in the original igneous or sedimentary rock source. Metamorphic rocks derived from ultramafic and mafic rocks average about 100 ppm Co; in contrast, gneissic granite contains only 16 ppm Co, and metasedimentary rocks average about 8 ppm. An exception to the general stability of cobalt during metamorphism is involved with the proposed origin of the sulfide deposits at Thompson, Manitoba, described briefly in a subsequent section.

Under oxidizing conditions, cobalt displays a strong tendency to concentrate with manganese (Rankama and Sahama, 1950, p. 650; Goldschmidt, 1954, p. 627, 632–642; Mason, 1958, p. 174; Goldberg, 1954; and Krauskopf, 1955). Mero (1965), describing the widespread occurrence of manganese nodules on the bottom of the Pacific Ocean, pointed out that MnO_2 precipitates as submicroscopic colloidal particles that "scavenge" any nickel, copper, cobalt, zinc, and molybdenum in the water. Cobalt is also abundant in residual soils derived from the deep weathering of manganiferous sedimentary rocks in a number of areas, particularly in the Eastern United States.

The concentration of cobalt, particularly with manganese oxides, and the separation of cobalt from nickel are especially pronounced in laterite deposits that occur over deeply weathered mafic and ultramafic rocks in tropical areas where rainfall is abundant (Engineering and Mining Journal, 1968). During the weathering process, magnesia and silica are leached downward or are removed. Nickel also migrates downward, whereas iron, manganese, cobalt, and alumina are residually enriched near the surface (Banning and others, 1962; Hotz, 1961; McMillan and Davis, 1955; and Pecora, 1944). In New Caledonia, the cobalt occurs in nodules, lenses, and small veins of cobaltiferous wad, or asbolane, commonly in a matrix of red iron-rich clay that does not contain appreciable nickel (Andrews, 1962, p. 187). In Cuba, both nickel and cobalt commonly occur in the same ore bodies.

COBALT MINERALS

Cobalt is a major or important constituent of approximately 70 minerals (Andrews, 1962, p. 6–12), and is a minor or trace constituent of several hundred more, particularly those containing Ni, Fe^{2+}, or Mn^{4+} (Fleischer, 1955). Minerals that are relatively high in cobalt and have been mined or concentrated for their cobalt content are listed in table 31. In addition, 27 cobalt sulfides, selenides, sulfosalts, and hydrated sulfates and arsenates contain relatively large amounts of cobalt, but are generally of such rare occurrence as to have no commercial importance. (See Fleischer, 1955; Fryklund and Fletcher, 1956; and Burnham, 1959.)

TABLE 31.—*Cobalt minerals*

Mineral	Percent cobalt
Linnaeite, Co_3S_4	58.0 (theoretical)
Siegenite, $(Co,Ni)_3S_4$	20.4–26.0
Carrollite, $(CO_2Cu)S_4$	35.2–36.0
Cobaltite, (Co,Fe)AsS	26.0–32.4
Safflorite, $CO,Fe)As_2$	13.0–18.6
Glaucodot, (Co,Fe)AsS	12.0–31.6
Skutterudite, $(Co,Fe)As_3$	10.9–20.9
Heterogenite, CoO(OH)	64.1 (theoretical)
"Asbolite," (Manganese oxides + Co)	.5–5.0
Erythrite, $(Co.Ni)_3(AsO_4)_2 \cdot 8H_2O$	18.7–26.3
Gersdorffite, (Ni,Co)AsS	(low)
Pyrrhotite, $(Fe,Ni,Co)_{x-1}S_x$	1.00 (maximum)
Pentlandite, $(Fe,Ni,Co)_9S_8$	1.50 (maximum)
Pyrite, $(Fe,Ni,Co)S_2$	13.00 (maximum
Sphalerite, Zn(Co)S	.30 (maximum)
Arsenopyrite, Fe(Co)AsS	.38 (maximum)
Manganese oxide minerals	.10–1.00 (or more)

TYPES OF DEPOSITS

Cobalt is recovered from mineral deposits both as a principal product and as a byproduct. Most of the world's supply of cobalt reaches the market as a byproduct of mining copper, nickel, and silver ores; smaller amounts are byproducts of iron, chromium, lead, zinc, uranium, and manganese. In this discussion of cobalt deposits, the geology will be emphasized, but the geologic features of specific cobalt deposits will be reviewed only briefly. Further information and references to many deposits are available in works by Vhay (1952), Andrews (1962), and Cornwall (1966), and in other chapters in this volume about commodities with which cobalt is associated.

Cobalt deposits may be classified geologically according to their environment of genesis or occurrence: (1) hypogene deposits associated with mafic intrusive igneous rocks; (2) contact metamorphic deposits also associated with mafic rocks; (3) lateritic (weathered) deposits; (4) massive sulfide deposits in metamorphic rocks, chiefly of volcanosedimentary origin; (5) hydrothermal deposits of several varieties; (6) strata-bound deposits; and (7) deposits formed as chemical precipitates.

HYPOGENE DEPOSITS ASSOCIATED WITH MAFIC INTRUSIVE IGNEOUS ROCKS

Commercial bodies of massive and disseminated

iron-nickel-copper sulfides containing cobalt are an important type of hypogene deposit associated with intrusive mafic igneous rocks. Large typical deposits of this kind occur in the famous Sudbury district of Ontario, where the ore has an average cobalt content of 0.07 percent (Andrews, 1962, p. 93). The suite of ore minerals consists of pyrrhotite, pentlandite, pyrite, marcasite, magnetite, cobaltite, and gersdorffite in pods, lenses, veins, stringers, and disseminated grains in a layered sequence of norite, quartz diorite, micropegmatite, and rocks of transitional composition and texture. The igneous host rocks of Precambrian age occur in an elliptical basin about 37 miles long and 17 miles wide. The ore deposits are large: A decade ago Andrews (1962, p. 93) reported proved reserves of more than 250 million tons of ore. The origin of these and similar deposits elsewhere in the world is complex and hotly debated. Cornwall (1966, p. 27–29) reviewed the hypotheses of origin ranging from segregation by differentiation in situ to hydrothermal deposition, and even to impact by meteorite. (See "Nickel.") More recently, Cheney and Lange (1967) have offered a summary of a process of sulfurization as an explanation of the origin of the Sudbury-type deposits of nickel and cobalt.

Deposits of the Sudbury type, however, are not restricted to Canada. Indeed, similar deposits are known in the United States, and some have been known for a long time. The Gap nickel mine, Lancaster County, Pa., is in the base of a metamorphosed gabbroic intrusive body. The ore is nickel-copper sulfide minerals that contain 0.1–0.3 percent cobalt. An estimated 1 million tons of ore remains at the old mine. Large deposits of this type also occur near Union, Maine, and in the keel of the Moxie Lake–Moosehead Lake gabbro body (Young, 1968, p. 129, 134). The huge deposits of the Katahdin Iron Works area are in gabbro and norite where the cobalt content of much mineralized rock is 0.05–0.1 percent. Samples from several bodies of mafic rock in the Calais area, Maine, indicate a cobalt content of 0.1 percent.

Cobalt is associated with pyrrhotite deposits in mafic rocks in Connecticut, at West Torrington and in the Mount Prospect area near Litchfield (Cameron, 1943), and in Massachusetts, at Dracut (Dennen, 1943). At the Phillips mine and vicinity near Peekskill, N.Y., gabbro of Precambrian age has mineralized rock that contains 0.003–0.24 percent cobalt. Other deposits of this type are reported in Washington, Oregon, and California.

Huge concentrations of copper-nickel sulfides occur in the lower part of the Duluth Gabbro Complex southeast of Ely, Minn. Samples from three drill cores contain 0.038 percent cobalt, 0.39 percent copper, and 0.14 percent nickel (Grosh and others, 1955). It is now estimated that about 14 billion tons of rock containing 0.25 percent total copper and nickel occur in a southwest trend 35 miles long (P. K. Sims, Director, Minnesota Geol. Survey, written commun., Sept. 22, 1972). No cobalt values are available for the large tonnage reported, but if the entire deposit contains an average of 0.01 percent cobalt—one-fourth of that reported in 1955—then about 3 billion pounds of cobalt would be available. Current knowledge of these deposits suggests that identified resources of 1 billion pounds of cobalt are a conservative estimate.

The mafic rocks of the Stillwater Complex in Montana contain some bodies of a few million tons rich in nickeliferous sulfides (Cornwall, 1966, p. 45–46) that also contain small amounts of cobalt.

Other cobaltiferous ores in large deposits are associated with mafic igneous rocks and metamorphic rocks in the Lynn Lake and Thompson–Moak Lake area, Manitoba. The deposits in the Thompson–Moak Lake area are of especial geologic interest because the nickel and cobalt probably were derived from peridotite and serpentine when they were metamorphosed at a temperature of at least 600°C to rocks of the garnet-amphibolite assemblage. Evidence suggests that sulfur was available in the hydrothermal solutions which deposited the mobilized nickel and cobalt in sulfide minerals, as first suggested by Michener (1957). If this process does indeed produce deposits of this type, peridotite bodies throughout the world could have valuable nickel-cobalt deposits if the bodies were sufficiently metamorphosed in an environment that had sulfur available. (See "Nickel"; also Cornwall, 1966, p. 20–23.)

CONTACT METAMORPHIC DEPOSITS

Deposits of magnetite, chalcopyrite, and cobaltiferous pyrite formed by contact metamorphism of carbonate rock by sills and dikes of diabase comprise an important type of cobalt deposit in the United States. Typical deposits are near Cornwall, Lebanon County, and Morgantown (the Grace mine), Berks County, Pa. These and many other deposits occur in the Triassic basin, an area about 75 miles long and 5–20 miles wide in southeastern Pennsylvania. At Cornwall, a discordant saucer-shaped body of diabase of Triassic age has silicated and mineralized adjacent carbonate rocks of Cambrian age. Recent descriptions of these commercially valuable iron deposits at Cornwall (Lapham, 1968) and Morgantown (Sims, 1968) indicate that the mine-run ore contains 0.02–0.056 percent cobalt, most of which is

concentrated in a pyrite-rich separate that contains 0.68–1.4 percent cobalt. About 75 percent of this cobalt is recovered and these mines are currently the major domestic source of cobalt. Some gold (1,700 oz in 1953) and silver also have been recovered from the pyrite concentrate at the Cornwall mine (Lapham, 1968, p. 79). The deposits in this region are large: The Cornwall mine alone has yielded nearly 100 million tons of ore since 1742.

LATERITIC DEPOSITS

Laterite, a mantle of internally weathered soil from a few feet to more than 100 feet thick, is formed over large areas of low relief during long periods of intense weathering and erosion, chiefly in humid subtropical to tropical climates. The weathering of peridotite and serpentine bodies generally yields a laterite rich in iron, nickel, cobalt, and chromium. The lateritic deposits commonly underlie many hundreds to many thousands of acres, and individual deposits may contain millions of tons of ore. Commercially valuable deposits contain 40–50 percent iron, 1–2 percent nickel, and 0.01–0.1 percent cobalt. Although the cobalt content of laterites is only one-tenth to one-fourteenth the nickel content, the cobalt can be recovered by chemical processing.

Cobaltiferous laterite deposits, many of Tertiary age, are scattered over the world, and resources include billions of tons of ore. Lateritic ores in the United States occur chiefly in California, Oregon, and Washington, and probably to a lesser extent in North Carolina. One of the largest deposits, near Riddle, Oreg., has reserves of 16 million tons of ore containing 0.05 percent cobalt (Vhay, 1969, p. 120). Smaller deposits containing 0.16 percent cobalt occur in the Webster district, North Carolina (Cornwall and others, 1968, p. 325).

Major lateritic iron-nickel deposits of the world occur in eastern Cuba where more than 2 billion pounds of cobalt occur in ore with an average content of 0.1 percent cobalt, 1.39 percent nickel, 2.75 percent chromium, and 38 percent iron (McMillan and Davis, 1955; Andrews, 1962, p. 149–150; Engineering and Mining Journal, 1968, p. 74). Other deposits of assorted sizes also occur in New Caledonia, the Solomon Islands, Indonesia, Australia, Philippines, Puerto Rico, Guatemala, Colombia, Venezuela, Brazil, U.S.S.R., Yugoslavia, Greece, and Malagasy Republic.

Closely allied to lateritic deposits are those chiefly in the eastern and central parts of the United States that have been derived from the weathering of manganiferous sedimentary rock. The deposits tend to be small. The cobalt content is more variable than in many nickeliferous laterites. The White Oak mine, Tennessee, contains 0.37–2.28 percent cobalt; the deposit at Round Mountain, Va., contains 0.12–2.24 percent cobalt; and the deposit at Rock Run, Ala., contains 0.05–4.8 percent cobalt. About 300,000 pounds of cobalt occur in deposits of this type in the southern Appalachian Mountains (Pierce, 1944, p. 270; Cornwall and others, 1968, p. 375). Manganese deposits of this type in Missouri contain over 1 million tons of ore in grade of 20 percent manganese and 0.5 percent cobalt at the contact of the Eminence and Gasconade Dolomites (Grawe, 1943). Cobalt also occurs in the manganese deposits of the Batesville district, Arkansas (Vhay, 1952).

Pierce (1944, p. 268) reported that the greatest cobalt concentrations in the manganese deposits of the southeastern States occur in those deposits containing the lowest concentrations of manganese. Experimental work has been done by the U.S. Bureau of Mines on chemically treating these manganese ores. When such beneficiation does become economically feasible, some cobalt and other metals present in small amounts can be recovered.

MASSIVE SULFIDE DEPOSITS IN METAMORPHIC ROCKS

Deposits of massive sulfides consisting chiefly of pyrite and pyrrhotite (some containing small amounts of cobalt) occur in metamorphic rocks. The host rocks commonly have andesitic composition and are probably of volcano-sedimentary origin. (See "Copper.") These deposits generally are mined for their content of sulfur, iron, copper, and smaller amounts of zinc, nickel, and cobalt.

Large massive sulfide deposits occur in the Blue Ridge and Piedmont provinces of the southeastern United States (Laurence, 1968, p. 162–164). The largest and best known of these deposits occur at Ducktown, Tenn. (Magee, 1968), where pyrite that contains 0.4–0.5 percent cobalt is reported by Cornwall, Vhay, and Frendzel (1968, p. 375). The cobalt currently is not recovered. The deposit at Sykesville, Md., contains base metals and some gold; the average content of cobalt is 0.07 percent (Heyl and Pearre, 1965). The en echelon bodies of primary pyrrhotite, chalcopyrite, and sphalerite along the 20-mile trend of the Gossan Lead, Carrol and Grayson Counties, Va., contain about 0.01 percent cobalt. At least 16 other deposits believed to be of the Ducktown type have been mined or explored from Carroll County, Md., southward to Randolph County, Ala., according to Laurence (1968, p. 164).

HYDROTHERMAL DEPOSITS

Hydrothermal deposits (formed from heated solutions) locally have been important sources of cobalt, and some of them are the only deposits mined chiefly for this metal. The hydrothermal deposits may be subdivided into two major classes: (1) vein deposits, and (2) replacement deposits.

In the United States, the vein deposits of the Blackbird district, Idaho, contain 1.6 percent copper, 0.6 percent cobalt, and lesser amounts of nickel and precious metals (Vhay, 1964, p. 68). The aggregate tonnage of the ore in the district was reported in 1959 to contain 15 million to as much as 225 million pounds of cobalt (Bilbrey, 1962, p. 27), equivalent to hypothetical resources in the classification of this report. In the Goodsprings district, Nevada, heterogenite forms envelopes around bodies of copper minerals. Large amounts of rock in many small bodies contain 0.3–0.5 percent cobalt (Vhay, 1952). Some cobalt occurs in the base metal veins of the Coeur d'Alene district, Idaho. Veins containing uranium, zinc, silver, nickel, and cobalt (0.09 percent) occur in the Blackhawk district, New Mexico (Gillerman and Whitebread, 1956). Several thousands of tons of cobaltian manganese ores (0.01–0.5 percent cobalt) occur in the Luis Lopez hot springs deposits, New Mexico. In Connecticut, veins with cobalt occur at Great Hill; and at the Booth mine, north of Bridgeport, at least two bodies of pyrrhotite contain 0.01 percent cobalt.

In Canada, veins that contain as much as 10 percent cobalt occur in the great silver-arsenide deposits of the Cobalt-Gowganda region, Ontario (Berry, 1971). Cobalt occurs with uranium in ore now produced in the Northwest Territories (Andrews, 1962, p. 99).

Many veins containing an average of 1.2 percent cobalt with nickel, iron, and silver occur in the Bou Azzer area, Morocco, near the contact of serpentinite and diorite with granite and mica schist of Precambrian age (Orcel and Jouravsky, 1936).

Hydrothermal replacement deposits containing cobalt minerals occur in the Bawdwin mine, Burma. The ore body consists of silver, lead, and zinc minerals that have replaced greatly sheared rhyolitic tuffs that are overlain and underlain by sedimentary rocks. The cobalt occurs in gersdorffite. The ore has an average grade of 0.5 percent cobalt, but during smelting of the ore the cobalt content is increased to 3–4 percent in the nickel speiss (Sharma, 1944). At Outokumpu, Finland, large reserves in a copper-rich sulfide deposit contain 0.2 percent cobalt, chiefly in the mineral linnaeite. The ore minerals replace quartzite, serpentinite, and other rocks of the Karelian schist (Vähätolo, 1953).

An extensive shear zone has been mineralized by small amounts of pyrite and sphalerite for at least 15–20 miles along the east foot of Catoctin Mountain, Va. Surface samples from about a half dozen localities along the strike suggest that although the grade of sulfide minerals is low, the distribution of the minerals is uniform. The cobalt content is 0.007–0.05 percent.

The geologic features of deposits of the Mississippi Valley type have been summarized recently by Snyder (1968, p. 277–284). The deposits occur chiefly in carbonate rocks of Cambrian to Pennsylvanian age on the flanks of broad domes. The ore consists mostly of sulfides of lead, zinc, iron, and copper. Sulfides of cobalt and nickel occur in a few districts. Fluorite and barite are major minerals in some districts, and minor in others. Cadmium, silver, germanium, and arsenic also are reported in some districts. All these ore materials probably were deposited from hydrothermal brines at temperatures not over 125°C.

The cobalt and nickel content of the Mississippi Valley ores is of particular interest because of the records of past production. At the south end of the old lead belt, especially in the Fredericktown and Mine La Motte areas of southeast Missouri, cobalt and nickel sulfides (siegenite, millerite, bravoite, and several unidentified minerals) associated with chalcopyrite and sphalerite locally were abundant, especially in places where the mineralized dolomite of the Bonneterre Dolomite pinches out against the Precambrian rocks in the core of the St. Francois Mountains (Kline and others, 1961). Siegenite-rich ores were the source of the cobalt produced in the southeastern part of the old lead belt in the early days of mining, as well as from 1944 to 1961.

The metal ratios in the ore of the Bonneterre–Flat River areas in the northern part of the old lead belt were estimated by Snyder and Gerdemann (1968, p. 349). The data indicated that cobalt and nickel were, respectively, 20 and 40 times more abundant than silver, but only the silver was recovered. Nearly all the 300,000 Troy ounces of silver produced in Missouri in 1965 came from the Bonneterre–Flat River area of the southeast district (Kiilsgaard, 1967, p. 71).

Cobalt and nickel sulfides associated with chalcopyrite and sphalerite are locally abundant in the lead deposits of the Viburnum Trend now in production on the west side of the St. Francois Mountains. These deposits also occur in the Bonneterre Dolomite in a belt about 27 miles long and have an average min-

able thickness of 20 feet (Snyder and Gerdemann, 1968, p. 334). The belt contains about 500 million tons of ore, if the average width of the minable zone is at least 150 feet (Gerdemann and Myers, 1972, p. 429). If the cobalt content of the raw ore is only 0.01 percent cobalt, the belt contains a resource of about 100 million pounds of cobalt.

Cobalt also occurs in the Wisconsin zinc district that includes adjacent parts of Illinois and Iowa. These ores, also of the Mississippi Valley type, include several cobalt minerals associated with pyrite, sphalerite, and some galena and chalcopyrite.

STRATA-BOUND DEPOSITS

Strata-bound deposits show pronounced stratigraphic localization in rocks of many different ages. One metal typically dominates, generally copper, lead, or zinc, and it is accompanied by lesser amounts of nickel, cobalt, silver, cadmium, and other elements. The great copper-cobalt deposits of Zaïre-Zambia are of this type; they occur in folded shale and dolomite that contain chalcopyrite, bornite, chalcocite, and a wide variety of other minerals, including linnaeite, carrollite, and others that contain cobalt. The ore bed, 20–80 feet thick, contains an average of 3.5 percent copper, but some ore contains 2 percent copper and 2 percent cobalt. These deposits currently are the world's major source of cobalt (Robert, 1956).

The copper-rich shales in the Kupferschiefer of central Europe formerly produced cobalt (Andrews, 1962, p. 123). The cobalt, copper, lead, zinc, and silver in this stratigraphic unit is a large resource that currently is mostly of subeconomic value.

CHEMICAL PRECIPITATES

Chemically precipitated cobalt is associated with the manganese nodules on the sea floor. Mero (1965, p. 235) estimated that such nodules in the Pacific Ocean, containing an average of 0.35 percent cobalt, are a resource of 5.8 billion tons of cobalt. Copper, nickel, and cobalt occur together in an average ratio of 3:4:1. Thus, cobalt produced from this source also would be a byproduct. (See also McKelvey and Wang, 1969.)

RESOURCES

The cobalt resources tabulated and discussed in this section have been selectively compiled from various published sources. Resources outside the United States were compiled only from the most readily available published data. Many of the details in the comprehensive compilations of world resources of cobalt by Vhay (1952) and Andrews (1962) have not been repeated here.

The totals of resources include materials containing 0.01 percent or more cobalt and are expressed in millions of pounds of cobalt. Resources of this grade already have yielded some commercial cobalt.

IDENTIFIED RESOURCES

The identified resources of cobalt in the United States are summarized in table 32. Most of the cobalt resources of the United States potentially are available only as byproducts of mining for the more abundant elements in the ores. The small production of

TABLE 32.—*Identified resources*[1] *of cobalt in the United States*

[+ = some identified resources]

State	Cobalt (millions of pounds)	Remarks
Alaska	125	Brady Glacier and other deposits (MacKevett and others, 1971).
Arkansas	+	Batesville manganese district.
California	25	Chiefly laterite deposits (Hotz, 1966, p. 283).
Idaho	50	Blackbird (Bilbrey, 1962, p. 27) and Coeur d'Alene districts (Vhay, 1964, p. 8).
Maine	130	Union and other deposits (Young, 1968), Katahdin Iron Works.
Minnesota	1,000	Sulfide deposits in gabbro, Ely area (Grosh and others, 1955).
Missouri	150	Southeast Missouri district (Kline and others, 1961), Viburnum Trend (Gerdemann and Myers, 1972).
Montana	+	Stillwater Complex, with chromium.
Nevada	+	Goodsprings district.
New Mexico	6	Blackhawk (Weber, 1965, p. 207–209) and other districts.
North Carolina	3	Chiefly laterite in the Webster district (Cornwall and others, 1968, p. 375).
Oregon	34	Chiefly laterite (Vhay, 1969, p. 116–120; Cornwall, 1966).
Pennsylvania	66	Contact metamorphic deposits in southeast region (Andrews, 1962, p. 161; Cornwall and others, 1968, p. 375).
Tennessee	40	Ducktown district (Magee, 1968, p. 234).
Vermont	+	Byproduct of talc operations (Andrews, 1962, p. 162; Vhay, 1952).
Virginia	25	Piedmont region; gossan lead and also includes Sykesville district, Carroll County, Md.
Washington	20	Chiefly lateritic ores (Vhay, 1966, p. 116–125).
Wisconsin	10	Upper Mississippi Valley district, includes adjacent parts of Illinois and Iowa.
Total	1,684+	

[1] Identified resources: Specific, identified mineral deposits that may or may not be evaluated as to extent and grade, and whose contained minerals may or may not be profitably recoverable with existing technology and economic conditions.

primary cobalt in the United States is more a function of economics and technological problems than the lack of ore deposits containing cobalt.

The most thoroughly evaluated deposits of cobalt in the United States contain more than 1.6 billion pounds of cobalt. That amount may soon be increased as the full potential of the great copper-nickel deposits in the Ely area, Minnesota, is evaluated. Although the ores might be considered marginal, technology is available to recover metal from this type of deposit. Development work has begun, and cobalt from these deposits may well reach the market before that from previously known deposits.

The mixed sulfide ores of the Mississippi Valley type are undoubtedly one of the great resources of cobalt and nickel in the United States. Reserves in the Madison mine, near Fredericktown, Mo., were estimated to contain another 14 million pounds of cobalt in 4.5 million tons of ore containing 0.16–0.18 percent cobalt (Kline and others, 1961). Most of these reserves and many other tons of cobalt resources on the east side of the St. Francois Mountains remain in the ground because old mining practices required that much of the ore with the highest cobalt content be left because of subsequent beneficiation and smelting problems. In 1949, it was estimated that 600,000 pounds of cobalt was lost annually from the lead ore processed in the district (Vhay, 1952, p. 45). By October 1972, all mining operations in the old lead belt on the entire east side of the St. Francois Mountains had ceased.

The world's identified resources of cobalt (table 33) are largely in the lateritic ores of the tropical regions. Production of nickel from laterite is expected to double by 1980, making additional supplies of cobalt increasingly available from this source (Engineering and Mining Journal, 1968, p. 73). It is clear, however, that large amounts of cobalt will continue to become available from other types of deposits, especially the sulfide deposits associated with mafic igneous rocks, as at Sudbury, Ont., and in the Ely area, Minnesota, and the strata-bound deposits of central Africa.

The minable reserves in the Bou Azzer area, Morocco, are now reported to be so small that mining may soon end (DeHuff, 1971, p. 401).

Not included in the world's total of cobalt resources in table 33 are those in the less conventional and less well evaluated deposits of manganese nodules on the sea floor. Mero (1965, p. 235) estimated that the manganese nodules in the Pacific Ocean alone contain 5.8 billion tons (11.6 trillion pounds) of cobalt.

TABLE 33.—*Identified resources [1] of cobalt in the world*

[+ = additional identified resources]

Country	Cobalt (millions of pounds)
Australia	650
Brazil	20+
Burma	35
Canada	550
Colombia	50
Cuba	2,312
Dominican Republic	196
Finland	50
Guatemala	100
Japan	6
Morocco	15
New Caledonia	850
New Guinea–Indonesia	40
Philippines	350
Puerto Rico	150
Solomon Island	50
Uganda	18
U.S.A.	1,684+
U.S.S.R.	400
Venezuela	132
Zaïre	1,500
Zambia	766
Total	9,924

[1] Identified resources: Specific, identified mineral deposits that may or may not be evaluated as to extent and grade, and whose contained minerals may or may not be profitably recoverable with existing technology and economic conditions.

HYPOTHETICAL RESOURCES

The world's hypothetical resources of cobalt are very large. Just as with the identified deposits, few of these deposits will be rich enough to mine for cobalt alone. Most of the world's future supplies of cobalt will reach the market as byproducts of other associated metals in greater demand, chiefly nickel, copper, iron, chromium, lead, zinc, precious metals, uranium, and manganese.

Hypothetical resources of cobalt in the United States probably amount to billions of pounds. Most of these resources are in various types of sulfide ore bodies.

Large resources already are postulated for the partly evaluated deposits in the gabbro near Ely, Minn. If the cobalt content of 0.038 percent (Grosh and others, 1955) is indicative of the grade of large volumes of rocks, then as much as 12 billion pounds of cobalt may be in these deposits.

The region around the Gap mine, Lancaster County, Pa., probably has not been prospected. The ore body at the Gap mine lies at the extreme west edge of an intrusive mafic complex containing an anorthositic core centered in the Coatesville area. Possibilities surely are favorable for the discovery of more deposits like the one at the Gap mine.

Possibilities for the discovery of more bodies of ore in Alaska similar to those already identified should be excellent. Other plutons containing nickel-cobalt-copper deposits may be found near some of

those already mentioned in the New England States.

Additional bodies of cobalt minerals associated with iron ore of contact metamorphic origin, such as those at Cornwall, Pa., probably lie hidden in southeastern Pennsylvania. Perhaps as many as two dozen bodies might occur at depth at the sites of magnetic anomalies in the region. The discovery of the hidden body that is now the Grace mine was facilitated by such data.

The chances for finding more massive sulfide bodies of the Ducktown type seem good all through the Appalachian region, especially in the southern Piedmont and Blue Ridge provinces.

Possibilities for the discovery of more ores of the Mississippi Valley type are good. The chances of such ore containing some cobalt and nickel seem favorable, because the ore already known in the midcontinental United States forms one of the world's great concentrations of metal sulfides, including cobalt and nickel, and two such cobalt-bearing districts, widely spaced, are known. Large deposits may still be found in extensions of known districts. The lead deposits of northern Arkansas might contain cobalt, especially indicated by the local bodies rich in pyrite. The known ore deposits may be the exposed parts of zoned districts in which the cobalt-rich parts are still hidden beneath barren caprocks.

Large new deposits of laterite probably will not be found in the United States. In many tropical areas of the world, however, substantially large hypothetical (and speculative) resources will likely be found, especially in some of the more remote regions.

More areas of sea bottom containing manganese nodules will be found and evaluated. When practical techniques for mining and extracting the metals from the nodules have been developed, large resources of cobalt will become available.

SPECULATIVE RESOURCES

The foregoing discussions suggest that the speculative resources of cobalt in the United States and the rest of the world are large.

Additional mafic and ultramafic rocks in the Appalachian and Cordilleran regions might be found containing valuable resources of cobalt. More massive sulfide bodies might be found at greater depth in Precambrian rocks of the Great Lakes region. Cobalt in commercial quantities might occur in large transverse veins in the copper region of the Upper Michigan Peninsula. In 1902 a shipment of arsenide minerals from the Mohawk mine went to the Camden Nickel Works and was "treated successfully" for cobalt, but records show no further production from that area.

Deposits of the Cornwall type may well occur along the edges of the diabase intrusions in the Triassic trough in Virginia, Maryland, and New Jersey. The Triassic region of New Jersey may well have more sills and lopolithic bodies at depth that are in contact with Paleozoic carbonate rocks that were most favorable for the formation of large ore deposits. Replacement deposits might occur along the diabase contact of the Triassic trough of the Connecticut Valley.

Additional districts containing cobalt-bearing sulfide ores of the Mississippi Valley type probably occur elsewhere in the United States and in the world. Geologic indications of such a district are exposed in the cobalt-bearing veins near Rossie, N.Y., and in nearby southern Ontario. These deposits do not seem to be related to the large zinc deposits of the Balmat-Edwards district, New York.

Metamorphic-hydrothermal deposits similar to those in the Thompson–Moak Lake district, Manitoba, probably occur elsewhere in the world. The possibilities are excellent in the great Precambrian Shield areas of Canada, Africa, Australia, and Eurasia for locating major ore districts of the Sudbury type, as has been shown by the many major discoveries since World War II.

PROSPECTING TECHNIQUES

Inasmuch as cobalt is produced chiefly as a by-product of mining other ores, relatively little direct exploration for cobalt deposits has been needed or undertaken, except during domestic national emergencies when foreign supplies were restricted or unavailable. These exploration efforts generally have been directed toward careful examination of areas of known cobalt deposits and occurrences using conventional geologic, geophysical, and geochemical techniques. Pyrrhotite deposits are particularly easy to identify by known geophysical techniques, and cobalt is easy to identify with geochemical prospecting methods. Techniques for determining trace amounts of cobalt are well known (Almond, 1953; Hawkes, 1957; Ward and others, 1963; Canney and Nowlan, 1964; Warren and others, 1964). Cobalt is more mobile than copper and may be useful as a pathfinder for deposits of associated elements (Canney and Wing, 1966). Biogeochemical prospecting for cobalt holds promise (Warren and Delavault, 1957; Tooms and Jay, 1964).

Applications of geochemical prospecting techniques have successfully found the extension of a vein in the Quartzburg district, Oregon, and outlined the Blacktail ore body as well as a large halo of cobalt in the Blackbird district, Idaho (Canney and

others, 1953). Methods are reported for special use in glacial areas (Koehler and others, 1954), in areas of deep soil in the tropics (Webb, 1958; Jay, 1959; Tooms and Webb, 1961), and in the study of secondary dispersion halos in the southern Ural Mountains of the U.S.S.R. (Makunina and others, 1962).

PROBLEMS FOR RESEARCH

Further geologic studies are needed on the minerals of cobalt and their genesis. Much needs to be learned about the mineralogy of cobalt so that better commercial separations and concentrations can be made in order to make better use of available resources of cobalt. The mineralogy of the sulfides of the Mississippi Valley type in Missouri has proved to be more complex than formerly realized and should be studied further. New and better technology is needed for the recovery of more valuable cobalt (currently selling for $1.85 per pound) from ores containing less valuable lead, zinc, and copper because loss of such valuable byproducts in mining, beneficiating, and smelting is not only a financial loss to the producer but, more importantly, may be an irretrievable loss of the material itself. A prime modern loss of cobalt is in the matte smelting of copper from deposits also containing lead and zinc, although techniques seem to have been available in the 19th century to recover much of the nickel and cobalt in the matte.

New technology needs to be developed to mine and recover cobalt and other metals from the manganese nodules on the sea floor. Methods developed in the laboratory to recover cobalt from supergene manganese oxides might be further advanced into commercial processes for cobalt recovery.

Another economically significant economic breakthrough would be the development of processes to recover cobalt and nickel from silicate minerals of ultramafic rocks whose average composition includes 0.027 percent cobalt and 0.19 percent nickel. Many cobaltiferous materials of potential commercial value contain less cobalt, but more nickel, than the average ultramafic rock. Dunite, because of its simple mineralogy, seems like a good material on which to begin intensive research.

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CONSTRUCTION STONE

By Robert A. Laurence

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ABSTRACT OF CONCLUSIONS

Domestic resources of stone for construction, both crushed and dimension stone, are adequate to provide for the expected demand indefinitely. Resource problems exist in localities of urbanization and industrial development and will increase, unless careful plans are made to reserve favorable areas for quarrying. Geologic mapping, especially of urban and suburban areas, can provide basic data for such planning.

INTRODUCTION

Stone is an essential mineral commodity in our modern industrialized society. It is especially important in building highways and railroads, but also has wide use in all phases of construction.

"Stone," as a commercial term, includes all consolidated rock used for construction and roads, as well as that used in cement manufacture, in agriculture ("aglime," poultry grit), in chemical and metallurgical industries, and for roofing granules. For purposes of this chapter, only stone used for construction, monuments, and roads is considered. Other uses of stone are discussed in the appropriate chapters.

Stone as a construction material may be further classified as crushed stone and dimension stone. Crushed stone is a term applied to rock that has been broken, crushed, or ground to smaller fragments after quarrying (Thrush, p. 284). Dimension stone is natural building stone that has been selected, trimmed, or cut to specified or indicated shapes or sizes (American Society for Testing and Materials, 1972, p. 103).

Desirable properties of stone for use as crushed stone in construction are toughness, strength, abrasion resistance, low porosity and absorption, and absence of minerals, such as sulfides or chert which may deteriorate through weathering or by chemical reaction with certain types of cement.

Desirable properties of dimension stone include those for crushed stone; in addition dimension stone must be free from fractures and other flaws so that it can be removed from the quarry in large blocks and then cut or shaped as desired. For most interior uses, dimension stone should be capable of taking a polish, and for both interior and exterior uses, the color and appearance of the exposed face are important characteristics.

PRODUCTION AND USE

According to Cooper (1970, p. 1219),

The stone industry is the largest nonfuel, nonmetallic mineral industry in the United States from the standpoint of total value of production and is second only to sand and gravel in volume produced. With exception of a few special varieties or qualities of dimension stone, the United States is

entirely self-sufficient with respect to stone requirements. Volumewise, imports and exports are approximately equal, but the value of imports, about $20 million in 1968, is appromiately double that of exports.

Use of dimension stone began when early man gave up nomadic life, and it flourished when early civilization built cities and temples. It is still an important industry—598 quarries produced $95 million worth of dimension stone in the United States in 1970 (Division of Nonmetallic Minerals, 1972, p. 141)—but United States production was highest in the 1920's, averaging about 4 million short tons annually between 1925 and 1930 (Currier, 1960, p. 15). Following a period of small production in the 1930's and early 1940's, production increased after World War II from less than 1 million short tons to 2½ million short tons in 1955, but has declined slightly since then.

The crushed stone industry began in England in about 1815 (Severinghaus, 1960, p. 285) and expanded rapidly after the invention of the mechanical rock crusher in 1858, especially during periods of extensive railroad and highway building. In 1969, more than 4,500 quarries in the United States produced 861 million short tons of crushed stone (Wood and Carrales, 1970, p. 16), with a total value of $1⅓ billion.

The recent, rapid growth of our domestic stone industry is shown by table 34. These figures, from the U.S. Bureau of Mines Minerals Yearbooks, show the tremendous increase in production of crushed stone, chiefly caused by demands of expanded highway and other construction, and the gradual decline of the dimension stone industry as use of concrete and steel for structural materials increased.

TABLE 34.—*Production of stone, United States*

[All figures are in millions]

		Dimension stone	Crushed stone	Total (rounded)
1929	Tonnage	4.7	93	98
	Value	$70	$94	$164
1939	Tonnage	2.3	145	147
	Value	$25	$133	$158
1949	Tonnage	1.8	222	224
	Value	$52	$289	$341
1959	Tonnage	2.3	145	147
	Value	$25	$133	$158
1969	Tonnage	1.9	861	863
	Value	$99	$1,326	$1,425
1970	Tonnage	1.6	873	875
	Value	$95	$1,380	$1,475

Imports in 1970 were valued at $35.7 million but amounted to only about 2.5 percent of the total value of stone consumed in the United States in that year. About 84 percent of the imported stone (by value) was dimension stone, chiefly marble from Italy and Portugal and granite from Canada and Italy. Total value of stone exports was $5.6 million—only 0.004 percent of the year's production (Drake, 1972). Prosperity of the stone industry does not depend on either exports or imports.

Demand is expected to increase, over the next 30 years, at an annual rate of 2.3–3.3 percent for dimension stone and 3.5–5.1 percent for crushed stone (Cooper, 1970, p. 1229).

DISTRIBUTION

Stone was produced in 1970 in all States except Delaware, and the total value of stone produced in the United States reached a new record high of $1.48 billion. More than 99 percent of the total quantity, with 93.5 percent of the total value, was crushed stone (Drake, 1972, p. 1). Stone was the principal mineral, by value, produced in eight States in 1970, was the second in 12 States, third in 10 States, and fourth in three (Daugherty and Fahrney, 1972, p. 6).

The eight most populous States produced 45 percent of the total output of stone, which represented 40 percent of the total value in 1970. This reflects, of course, the importance of the cost of shipping or hauling stone from the quarry site to the place of use. Inasmuch as the present heavily populated areas will continue to be the principal areas of growth and construction, they will continue to be the leading consumers of construction materials, and a healthy and adequate stone industry must be maintained in and near all major population centers. Nearly three-fourths of all crushed stone produced in the United States in 1970 was shipped by truck (Drake, 1972, p. 15). After a very few miles, the cost of trucking can exceed the total of all other production costs of crushed stone.

Most kinds of rock are suitable for use as crushed stone; as a result no area in the United States is far from an active or potential source of crushed stone. Distribution of these sources of stone is shown in figure 18. About 73 percent of the total output of crushed stone, which represents 67 percent of the total value, is limestone; traprock and granite are the other principal varieties produced (table 35).

Distribution of types used for dimension stone is shown in figure 19. Granite is the leading variety representing 37 percent of the total output and 46 percent of the total value; limestone and sandstone are next in abundance (table 35).

The principal competitor of and substitute for crushed stone is another ubiquitous mineral commodity, sand and gravel. It is commonly used as a substitute for stone in road construction and as concrete aggregate. Usually, the availability and

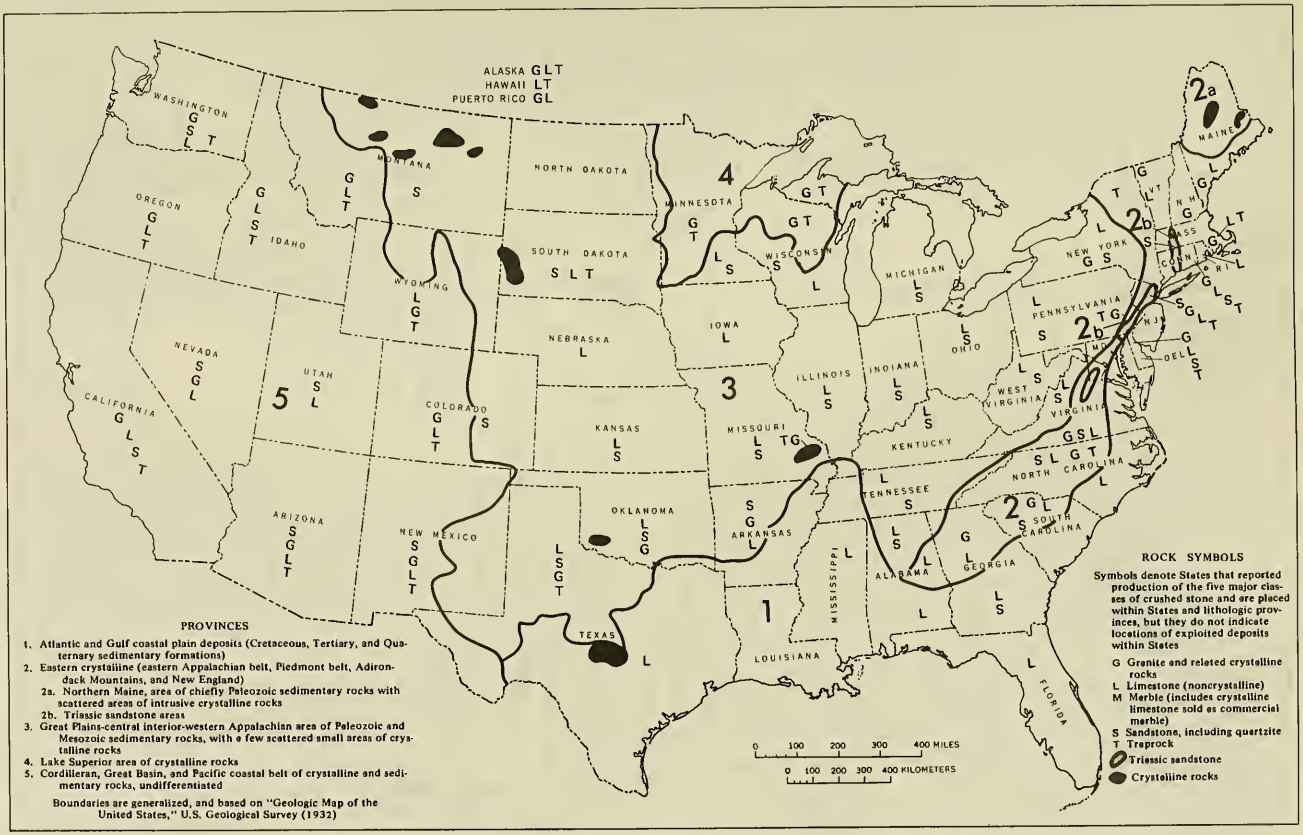

FIGURE 18.—Lithologic provinces of the United States as related to occurrence and production in 1969 of principal kinds of crushed stone. Modified from Currier (1960).

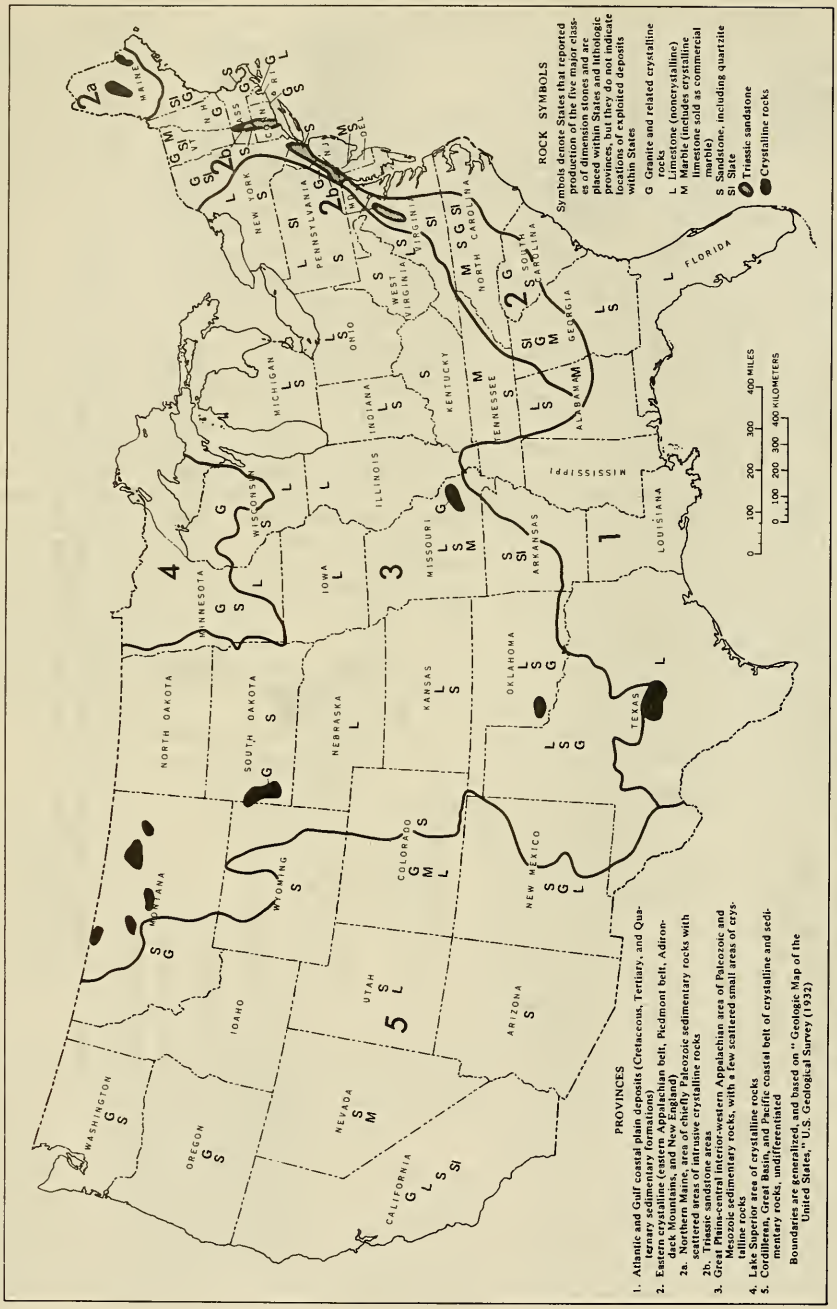

FIGURE 19.—Lithologic provinces of the United States as related to occurrence and production in 1969 of principal kinds of dimension stone. Modified from Currier (1960).

TABLE 35.—*Production of stone in 1969, by types of stone, in the United States*

Type	Percentage of total	
	Tonnage	Value
Crushed stone		
Limestone (including dolomite)	73	$67
Granite	9	9
Marble	.2	2
Sandstone (including quartzite)	3	4
Traprock	10	11
Other	4.8	7
	100	100
Total ——millions—	861	$1,326
Dimension stone		
Granite	37	$46
Limestone (including dolomite)	31	18
Marble	4	13
Sandstone (including quartzite)	17	11
Slate	8	9
Other	3	3
	100	100
Total ——millions—	1.873	$99

cost of transportation determine which of the two is used in any particular job; these qualifications depend upon local features. In areas which have been glaciated (for example, the Ohio Valley and the Great Lakes) or in coastal-plain areas, consolidate rock may be scarce or may be covered by unconsolidated materials, giving the latter products a competitive cost advantage.

Other substitutes for crushed stone are manufactured aggregates, such as slag or expanded lightweight aggregates.

Principal substitutes for dimension stone are precast concrete slabs or blocks (which may use either crushed stone, sand and gravel, or expanded shale as aggregate), bricks, and glass or ceramic products. Use of dimension stone as a principal structural material has declined since the growth of structural steel construction, but many producers are now providing dimension stone in thin slabs or as composites, with concrete backing, for exterior use (Bliss, 1971), and a growing demand is anticipated.

PROBLEMS FOR RESEARCH

Although the United States is self-sufficient in resources of stone, local problems commonly result from lack of adequate planning to reserve the best areas for quarrying. Many communities expanded so rapidly during the 1950's and 1960's that potential quarry sites were surrounded, or in some cases covered, with urban development. Then, when existing quarries approached property lines, or encountered excessive water which increased the cost of deeper quarrying, the operators had difficulty in locating and developing a new site. Residents object to the noise, vibration, blasting, dust, and increased truck traffic associated with quarrying. To avoid this, operators have had to go to more distant sites, thereby increasing the cost of the delivered product. One alternative to this is underground quarying, which has the additional advantage of providing usable underground space after the rock has been removed. An example is a 1,500-acre tract in Kansas City, Mo., where the planned use as an underground storage area serves as a guide in the extraction of limestone (Missouri Geological Survey and Water Resources, 1970).

In most areas, certain geologic formations provide the best source of stone for construction. If a geologic map of the area has been made, it is a simple matter to prepare a map showing areas of suitable quarry rock which should be preserved, and these could be of great assistance to zoning boards, planning commissions, and other nongeological groups who are faced with the problem of locating construction stone.

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COPPER

By Dennis P. Cox, Robert G. Schmidt, James D. Vine, Harold Kirkemo, Elizabeth B. Tourtelot, and Michael Fleischer

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ABSTRACT OF CONCLUSIONS

About 70 percent of the world's identified copper resources can be grouped in the following geologic-geographic categories, listed in order of decreasing importance: porphyry copper deposits of Chile and Peru, porphyry copper deposits of the Southwestern United States (19 percent of the world total), sedimentary copper deposits of Zaïre and Zambia, and porphyry copper and sedimentary copper deposits of the U.S.S.R. Other important groups of identified resources include porphyry copper deposits in Oceania, in Mexico, and in western Canada and porphyry copper and sedimentary copper deposits in southeastern and central Europe, respectively. These and the remaining identified resources amount to 344 million tons of copper metal, sufficient to last for 50 years at present rates of mine production.

Hypothetical resources, or those not now known but suspected to be present near known deposits, will probably provide another 400 million tons of copper. Important resources of this category are most likely to occur in the porphyry copper provinces of southeastern Arizona, western Canada, Chile, and Peru. Large sedimentary deposits will probably be found in Africa, the U.S.S.R., and the northern Rocky Mountains of the United States. Additional resources in sea-floor manganese nodules also will probably be discovered.

It is possible to speculate that another 320 million tons of copper might be found in areas not yet prospected and in which important deposits are unknown. The most promising areas lie in the Basin and Range province of the United States, outside the known porphyry copper province; in the U.S.S.R. Far East where porphyry copper provinces may be found in Mesozoic fold belts and the younger island arc system; and in the Brazilian shield where major sedimentary copper deposits might be found.

The aforementioned identified, hypothetical, and speculative categories refer to known or postulated ore deposits, minable under present economic and technological conditions. In addition to these are large conditional resources in porphyry copper, sedimentary copper, and igneous copper-nickel deposits and in manganese nodules on the sea floor. At least 381 million tons of copper in such subeconomic deposits can be identified or hypothesized. This copper may become available at some future period of high metal prices and (or) improved technology.

A comparison of current U.S. and world production and the copper content of various copper deposits shows that the United States produces enough copper to mine out an average-sized porphyry copper deposit each year. Maintaining a balance between deposits discovered and deposits mined out means that a great investment in geological, geochemical, and geophysical studies must be made and maintained in spite of short-term fluctuations in the price of copper.

PROPERTIES, USES, AND RESOURCES

Copper, one of the most useful and versatile metals, has been used by man perhaps longer than any other metal except gold. Its unique physical and mechanical properties are utilized both in its metallic state and in alloy with many other metals. Copper, chemical symbol Cu, has a hardness (Mohs' scale) of 2.5–3, a melting point of 1,083°C, a boiling point of 2,595°C, a density (annealed at 20°C) of 8.89, and an electrical resistivity at 20°C of 1.71. Its electrical conductivity in cross section and by weight is surpassed only by silver and by aluminum, respectively.

High electrical and thermal conductivities, good resistance to corrosion, good ductility and malleability, high strength, lack of magnetism, and a pleasing red color are properties and characteristics of copper that find innumerable industrial applications. Copper and many of its alloys can be joined by welding, brazing, and soldering. It can be finished by plating and lacquering.

The four traditional copper-base alloys, brass, bronze, nickel-silver, and cupronickel, contain no less than 40 percent copper, with the amount of copper not less than that of any other constituent. Copper also is used in many other alloys where it is not the major component.

About half (53 percent) of the 1.5 million tons of copper used domestically in 1970 was for electrical applications, followed by 16 percent in construction, 12 percent in industrial machinery, 8 percent in transportation, 6 percent in ordnance, and 5 percent in other uses.

Use of copper in all applications for which it is suited would exceed its available supply, but aluminum has substituted for copper in many applications. In the last two decades U.S. consumption of aluminum has more than tripled, while the use of copper increased only 15 percent. Although copper is virtually indispensable for some applications, aluminum serves satisfactorily as an alternate metal in many others, and often at lower cost. The relative capabilities of the two metals in their electrical conductor applications depend on their physical and mechanical properties. For example, an aluminum conductor weighs only 30 percent as much as a copper conductor of identical size, but an aluminum conductor has 1.64 times the electrical resistance of a copper conductor of equal size. Thus, for equal current-carrying capacity, an aluminum conductor weighs half as much as a copper conductor, but has a cross-sectional area 26 percent greater.

Aluminum and stainless steel are used in place of copper for some applications in the building industry. Steel increasingly replaces brass in shell cases. The use of copper cladding proportionately requires less copper than would solid copper; copper now substitutes for silver in coins which have a copper core and a cupronickel cladding material. Printed electrical circuits and plastics have replaced copper in many applications. These shifts in the overall use pattern make more copper available for preferred uses. In spite of substitution, the continued use of a substantial part of our present copper requirement is needed to maintain or present living standard.

The supply to meet domestic demand is derived from U.S. mine production, secondary production (recovery of old scrap), imports, and withdrawals from industrial and Government stockpiles. The trends in supply and demand for copper during the period 1950–70 are illustrated in figure 20 and table 36. Other demand forecasts to the year 2000 are discussed by Lowell (1970) and by Ageton and Greenspoon (1970).

Copper is traded in a number of commercial classes—ore, concentrate, matte, blister, refined, and secondary—each with varying percentages of copper content. Because of the complexity in determining the total amount of copper used from all classes and the many demands of trade such as imports, exports, and stockpiles, the total demand

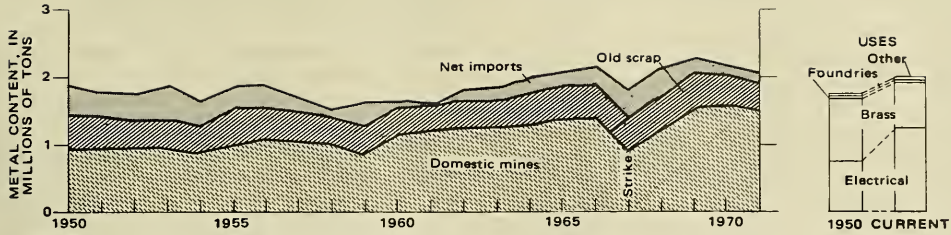

FIGURE 20.—U.S. supplies and uses of copper, 1950–71. (From U.S. Department of the Interior (1972).

TABLE 36.—*Copper supply and demand data, 1950–71, and projections for the year 2000, in thousands of short tons*

[Data from National Commission on Materials Policy (1972), U.S. Department of the Interior (1972), and U.S. Bureau of Mines (1970)]

Year	Refined production U.S. mines	Old scrap	U.S net imports	Total U.S. demand, exclusive of new scrap	Rest of world mine production
1950	921	485	491	1,897	1,851
1960	1,121	429	107	1,657	3,570
1970	1,521	504	155	2,180	4,847
1971[1]	1,400	450	190	2,040	(2)
2000[3]	2,380	1,700	(2)	9,700	(2)

[1] Preliminary.
[2] Not available or estimated.
[3] Unrefined.

often is expressed as withdrawals or apparent consumption.

With few exceptions, the United States has been a net importer of copper each year since 1939. Dependency on foreign sources of supply has ranged from a high of about 60 percent in 1945 and 1946 to 6 percent in 1971.

The major sources of copper imports in 1971 were Canada, 37 percent; Peru, 29 percent; Chile, 15 percent; and all other countries; 19 percent. Major destinations of copper exports in 1971 were West Germany, 26 percent; Italy, 11 percent; France, 10 percent; Canada, 9 percent; and all other countries, 44 percent.

The sources of 1971 imports differ markedly from the sources for the 1967–70 period, when 27 percent originated in Chile, 23 percent in Canada, 21 percent in Peru, 7 percent in the Republic of South Africa, and 22 per from all other countries. The nationalization in 1971 of mines owned by U.S. firms in Chile disrupted world trade patterns in copper, as is evident from the preceding data.

The possible effect of industrialization of developing countries on the world copper market is best illustrated by the Peoples Republic of China. Present per-capita copper consumption in China is about one-half pound per year, and many recent studies of the world metal situation have pointed to the impact of the increase that is sure to come with advancing industrialization in that and other populous, mostly agricultural, countries. Even though Chinese copper production may increase rapidly, consumption may well outrun it for many years, and China probably will become a major importer in the short term, though self-sufficiency may be possible at a future time. The 4-year agreement for Chinese purchase of copper from Chile is an example of this kind of change that is sure to have widespread effect on the world copper market.

EXPLOITATION

The introduction of new domestic sources of copper, important new developments, and other events having significant impact on the supply of copper are shown in relation to primary copper production in figure 21.

Development of foreign deposits also has had its impact on the copper industry. The more economically important developments were the following:

1912, Braden Copper Co. began operations in Chile.
1916, Chile Copper Co. started production at Chuquicamata.
1924, Katanga in Zaïre (Congo) started production.
1950, 1960's, Large deposits developed in Chile and Peru. Substantial production started and reserves added in Canada, Zambia, Zaïre, Yugoslavia, Poland, Ireland, Finland, Bulgaria, U.S.S.R., Australia, and the Philippines.

Among the foreign developments begun in the 1960's and expected to be in production in the 1970's are those in Indonesia (West Irian), New Guinea (Manus Island, Bougainville), British Columbia, and Iran.

Two factors of paramount importance to the copper industry are the grade of ore mined and the price per pound. The steady decline in average grade of domestic ore mined and the wide range in prices are evident in the following summary:

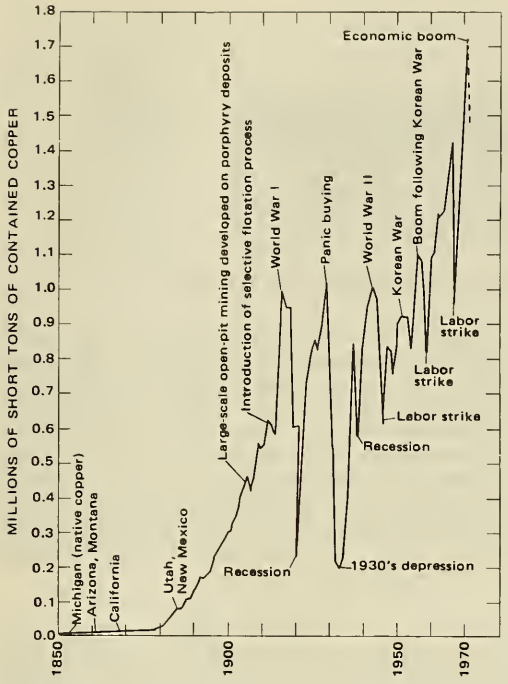

FIGURE 21.—U.S. primary copper production, 1850–1970. Notes indicate major new sources, developments, or events.

Year	Average annual price in cents per pound Quoted refinery	Equivalent 1970 dollars	Average grade of ore mined (percent copper)
1900	16.19	63.5	4.0
1910	12.73	43.5	1.88
1920	17.45	30.0	1.63
1930	12.98	32.5	1.43
1940	11.29	29.5	1.20
1950	21.32	30.0	.89
1955	37.49	41.0	.83
1960	32.05	36.5	.73
1965	35.02	39.9	.70
1970	58.20	58.2	.60

Copper ores also contain other valuable recoverable metals, and many ores mined chiefly for other metals also contain recoverable copper. The coproduct-byproduct recovery of copper and associated metals from ores depends upon the quantity of metals present (grade) and the processes used in recovering the principal values. Copper production yields significant quantities of gold, silver, molybdenum, cobalt, zinc, lead, nickel, sulfur, tellurium, selenium, rhenium, palladium, platinum, arsenic, and iron. Selenium is an essential byproduct of copper production, and rhenium is obtained from the molybdenum in porphyry deposits. Cobalt is derived mainly from copper ores mined in Zaïre.

Several problems of major concern to copper producers relate to protecting environmental qualities while maintaining competitive costs. Copper smelters are under severe new or proposed restrictions on sulfur emission, requiring major capital investment for control equipment. This stress may result in the closing of some smelters and a shift to new methods of hydrometallurgy. Surface restoration is particularly difficult in copper mining because of the finely powdered state of mill tailings and the very high ratio of waste to produced metal. Water pollution by mine and mill waste is a problem, and particularly as many of the big copper deposits are in arid regions, obtaining adequate water supplies for mining and milling becomes more difficult.

Several porphyry copper deposits in Arizona are now being worked by in-place leaching methods which greatly decrease the effect of copper extraction on the environment. The deposits are first cut by a system of tunnels, then fractured by explosive or hydraulic methods, and then leached by sulfuric acid introduced through pipes to the upper part of the deposit. The copper-rich fluids are withdrawn from the lowest levels of mine workings, pumped to the surface and the copper removed electrolytically. The main disadvantages of this method are that only 50–60 percent of the copper in the ore deposit can be recovered under present techniques, and that all of the byproduct metals, such as molybdenum, gold, and selenium, are left in the rock during the leaching process.

GEOLOGIC ENVIRONMENT

GEOCHEMISTRY AND ABUNDANCE

Copper is a chemical element of group II–B of the periodic table; it has atomic number 29 and atomic weight 63.546, consisting of the isotopes ^{63}Cu (69.09 percent) and ^{65}Cu (30.91 percent). It occurs in nature as the native element, as compounds of Cu^{+1} (ionic radius 0.54 A) and Cu^{+2} (ionic radius 0.81 A for sixfold coordination). In the Cu^{+2} state, as shown particularly by naturally occurring sulfates and phosphates, it is isomorphous with Zn (0.83 A), Mg (0.80 A), and Fe^{+2} (0.69 A). In sulfides, Cu^{+2} is isomorphous with zinc (as in tetrahedrite), and Cu^{+1} with silver. Copper is a strongly sulfur-seeking (chalcophile) element, and it tends to be concentrated in sulfide deposits; in igneous rocks it occurs mainly as finely divided sulfides, principally chalcopyrite and bornite.

Estimates of the abundance of copper in the con-

tinental crust have been reviewed by Parker (1967); most recent estimates are about 50 ppm (parts per million). As indicated in table 37, copper is concentrated in the igneous cycle in basaltic and gabbroic rocks. In these it is highest in the ferromagnesian minerals such as pyroxenes and biotite where it probably occurs mainly as minute grains of chalcopyrite (Goldschmidt, 1954, p. 182).

TABLE 37.—*Copper content of various materials*

Type of material	Copper content generally reported	
	Range	Average
Igneous rocks (parts per million)		
Ultramafic rocks	------	15
Basaltic and gabbroic rocks	30–160	90
Andesites	------	35
Granitic rocks	5–30	15
Sedimentary rocks (parts per million)		
Limestones	------	4
Sandstones	[1] 10–20	10(?)
Shales and clays	18–120	[2] 45
Soils	2–100	20
Phosphorites	10–100	30
Coals	2–40	15
Waters (parts per billion)		
Sea Water	1–15	3
Surface waters	.4–150	5(?)

[1] Pettijohn (1963).
[2] 250 for deep-sea clays (Turekian and Wedepohl, 1961); 560 average for 450 samples of deep-sea clay (Landergren and Manheim, 1963).

During the crystallization of igneous rocks, copper and some other elements that do not fit readily into the structures of silicate minerals may be concentrated to form ore deposits. If the magma contains appreciable volatiles, copper may be dissolved and transported with these into veinlets or extensive vein systems. If, as in the case of some gabbroic rocks, the volatile content is low, copper may remain in the intrusion, concentrating as an immiscible copper sulfide fluid.

The data on sea water indicate that less than 0.1 percent of the copper carried to the ocean remains in solution, the remainder being precipitated—mainly with the clays, in part with manganese oxides, and in part removed by biota. Probably much, perhaps most, of the copper reported in surface waters is due to industrial contamination from metallurgical wastes, plating work, and so forth.

Copper is found in at least trace amounts in nearly all sedimentary rocks. The averages for some common rocks are shown in table 37. The copper content of Lower Eocene nonmarine sandstones in the Rocky Mountain region was found to average 11 ppm and, for individual basins, to range from 5.2 to 29 ppm (Vine and Tourtelot, 1970a). Pelitic Belt rocks from the Mission Mountains Primitive Area, Mont., contain an average of 14 ppm copper, whereas similar rocks in the Pend Oreille, Idaho, area contain 6.8 ppm copper (Harrison and Grimes, 1970, table 11).

Copper is readily soluble and mobilized by oxidizing solutions; therefore, it concentrates in certain environments of deposition. Thus, marine clays and other fine-grained rocks tend to have more copper than coarse-grained rocks and limestones. Moreover, the average black shale contains about twice as much copper as the average shale, and some black shales rich in organic matter contain several hundred parts per million copper (Vine and Tourtelot, 1970b). Pelagic sediments contain significantly greater concentrations of copper than continental rocks. Landergren and Manheim (1963) reported 560 ppm copper as the average for 450 samples of deep-sea clay. Bostrom and Peterson (1966) found more than 1,000 ppm copper and an enrichment of several heavy metals along the crest of the East Pacific rise. A metal-rich sediment associated with hot brine from the Atlantis II deep in the Red Sea is reported to contain 0.5 percent copper (Miller and others, 1966).

GEOCHEMICAL CYCLE

Copper is introduced into the accessible part of the earth's crust from unknown deeper sources by igneous intrusions and by upward migrating fluids. Economic concentrations of the metal may result directly from these processes and from secondary effects of weathering, erosion, and sedimentation. Remobilization and reconcentration by numerous later stages of intrusion and by metamorphism may occur, and in addition ground water and deep connate waters may dissolve, transport, and redeposit copper to form younger ore deposits. Copper in oceanic basalt and copper carried to the sea in solution and deposited with oceanic sediments may be remobilized during subduction of oceanic crustal plates, and a part may ultimately be redeposited in continental crustal rocks above the subduction zone.

The weathering of chalcopyrite readily oxidizes copper and releases it to ionic solution. A portion of this ionic copper may be adsorbed on organic matter, clay minerals, and iron oxide particles, and some of it probably reaches the sea in ionic form. According to Robert Ehrlich and T. A. Vogel (oral commun., 1972), the absence of much potassium is an important factor in the transport of copper as a complex with montmorillonite. The copper in solution in river waters ranges widely, but 0.010–0.015 ppm is probably the general range for large rivers. Some copper is believed to have been transported to the Siberian Udokan deposits in detrital form

(Bogdanov, 1968), and Ehrlich and Vogel (oral commun., 1972) suggested that some of the copper in the Nonesuch Shale was carried in this way.

Because sea water contains only 0.003 ppm copper (Green, 1969), the discharge of an estimated 1×10^6 tons new copper by streams each year must be balanced against various mechanisms that remove it. In reducing environments, copper is probably precipitated as the sulfide by sulfur-reducing bacteria or adsorbed on decaying humic organic matter. Copper also accumulates in some oxidizing environments, such as in manganese nodules and in pelagic muds where precipitation may occur as the oxide. The fate of copper in an evaporite environment is not understood. Some copper may be concentrated in residual brines and eventually squeezed into adjacent porous sediments and precipitated by reaction with hydrogen sulfide. Copper may also be trapped in connate pore waters in basins of nonmarine deposition. Precipitation would eventually occur by reaction with hydrogen sulfide or organic matter, or as a carbonate, sulfate, silicate, or phosphate. The regional and stratigraphic association of strata-bound copper ores with evaporites was described by Davidson (1965).

Prior to the evolution of a modern atmosphere containing about 20 percent oxygen some 1.2–1.4 billion years ago (Cloud, 1971), the geochemical cycle for copper may have been significantly different. Primary copper sulfide minerals were probably sufficiently stable to survive weathering and redeposition as heavy minerals in detrital rocks. Subsequent exposure of buried sediment to oxygenated waters could have resulted in redistribution of the copper in chemically reactive environments within the sedimentary sequence, for example in beds rich in organic matter.

MINERALOGY

Copper occurs in at least 160 minerals. Table 38 gives the name, composition, and general mode of occurrence of 20 of the more common ones.

Chalcopyrite is by far the most abundant copper sulfide; bornite and chalcocite are next in abundance. The sulfarsenides enargite and tennantite and the sulfantimonides tetrahedrite and famatinite are generally rare, but each makes up major parts of at least one large ore body. The mineral digenite ($Cu_{2-x}S$) is not shown in table 38, but it may be a major ore mineral. It is detected only by careful petrographic work or X-ray analysis and is generally reported as chalcocite. Native copper is abundant in certain types of deposits.

Malachite, azurite, and chrysocolla are the most

TABLE 38.—*Minerals of copper; composition and environment of origin*

[o, major ore mineral; x, minor ore mineral]

Name	Composition	Porphyry	Vein and replacement	Sedimentary strata-bound	Volcanogenic strata-bound	Magmatic segregation	Keweenaw type	Secondary enrichments and secondary deposits: Oxide zone	Secondary enrichments and secondary deposits: Sulfide zone
Major minerals									
Native copper	Cu	--	--	o	--	--	o	x	x
Chalcocite	Cu_2S	--	o	o	o	--	x	--	o
Covellite	CuS	--	--	--	--	--	--	--	o
Bornite	Cu_5FeS_4	x	o	x	o	o	--	--	--
Chalcopyrite	$CuFeS_2$	o	o	o	o	o	--	--	--
Enargite	Cu_3AsS_4	o	o	--	x	--	--	--	--
Cuprite	Cu_2O	--	--	--	--	--	--	o	x
Malachite	$Cu_2(OH)_2(CO_3)$	--	--	--	--	--	--	o	--
Significant supplementary minerals									
Tetrahedrite	$(Cu,Fe)_{12}Sb_4S_{13}$	--	x	--	x	--	--	--	--
Tennantite	$(Cu,Fe)_{12}As_4S_{13}$	--	x	--	x	--	--	--	--
Famatinite	Cu_3SbS_4	--	x	--	--	--	--	--	--
Stannite	Cu_2FeSnS_4	--	x	--	(?)	--	--	--	--
Atacamite	$Cu_2(OH)_3Cl$	--	--	--	--	--	--	x	--
Tenorite (melaconite)	CuO	--	--	--	--	--	--	o	--
Azurite	$Cu_3(OH)_2(CO_3)_2$	--	--	--	--	--	--	x	--
Chrysocolla	$CuSiO_3\cdot2H_2O$	--	--	--	--	--	--	o	--
Brochantite	$Cu_4(SO_4)(OH)_6$	--	--	--	--	--	--	x	--
Antlerite	$Cu_3(SO_4)(OH)_4$	--	--	--	--	--	--	o	--
Chalcanthite	$CuSO_4\cdot5H_2O$	--	--	--	--	--	--	o	--
Kroehnkite	$Na_2Cu(SO_4)_2\cdot2H_2O$	--	--	--	--	--	--	x	--

common minerals of the oxidized zone, and the bright colors of these minerals have been a guide to prospectors for thousands of years.

TYPES OF DEPOSITS

Most copper deposits fall into one of five major types. (1) The most important of these are the porphyry copper deposits and vein and replacement deposits; these account for almost two-thirds of the world's copper resources and are discussed together because of their common genetic association with felsic intrusive rocks. (2) A fourth of the world's identifiable copper resources is in sedimentary rocks, and (3) about 5 percent is in volcanic rocks as massive sulfide deposits. (4) Smaller portions of world resources are in nickel-copper ores formed by magmatic processes in mafic intrusives and (5) in native copper ores of the Keweenaw type. These types, as well as certain uncommon or unique types of deposits, are discussed in order of their relative importance as copper resources.

PORPHYRY COPPER DEPOSITS AND RELATED TYPES

Porphyry copper deposits and most of the important vein and replacement copper deposits are genetically associated with intrusions of felsic igneous rocks. The copper in these deposits is believed by some geologists (for example, Fournier, 1967) to be a primary constituent of the associated intrusion. A part of the copper is trapped in disseminated grains by the rapid crystallization of the magma, which in turn gives rise to the characteristic porphyritic texture of the intrusion. Another part of the copper is mobilized by water and other volatiles escaping from the hot congealed rock mass and is deposited in fractures in the intrusion and its wall rocks. A third part may escape completely from the intrusion and form vein and replacement deposits in nearby reactive host rocks. Thus porphyry copper deposits commonly occupy the central part of large or small mining districts containing vein and replacement deposits of copper, lead, zinc, silver, gold, iron, and manganese.

PORPHYRY COPPER DEPOSITS

An excellent review of the geology of porphyry copper deposits of the North American Southwest with detailed descriptions of 15 individual deposits was assembled by Titley and Hicks (1966). Sutherland-Brown (1969) and Sutherland-Brown, Cathro, Panteleyev, and Ney (1971) wrote excellent descriptions of deposits in British Columbia.

Porphyry copper deposits are defined herein as deposits of disseminated copper sulfide that are in or near a felsic intrusive body; in most deposits, at least one facies of the intrusive is a porphyry. This definition does not include size, grade, or amenability to mass-mining methods because these factors restrict consideration of the similar but subeconomic occurrences that are so important to regional metallogenic studies. Lowell and Guilbert (1970) tabulated the geologic features of 27 major porphyry deposits, 18 of them in the North American Southwest, and arrived at a typical or average deposit. This hypothetical ore body is oval and pipelike, it measures 3,500 by 6,000 feet in plan, and it contains 150 million tons of ore averaging 0.8 percent copper and 0.15 percent molybdenum. Ore below the zone of secondary enrichment contains on the average only 0.45 percent copper. On the average 70 percent of the ore body is in the intrusion, and 30 percent is in the country rock. Sulfide minerals in descending order of abundance are pyrite, chalcopyrite, molybdenite, and bornite. Supergene sulfides may form a higher grade zone of secondary enrichment.

Porphyry copper deposits have petrologic associations that are dependent on their tectonic environment. Deposits formed on thick continental crust are usually associated with quartz monzonite, as in Arizona (Lowell and Guilbert, 1970). Deposits in island arcs are associated with quartz diorite, diorite, or granodiorite, as in Bougainville (Macnamara, 1968), the Philippines (Madamba, 1972; Loudon, 1972), and Puerto Rico (Cox, 1971). Similarly, British Columbia porphyry deposits of two distinct ages and of distinct petrologic affinities seem to be related to two types of crustal plate motion (Hodder and Hollister, 1972). Thus, deposits of Triassic and Jurassic age were formed during plate convergence as the North American plate moved westward over the Pacific plate; as the East Pacific rise drifted under the American plate, development of tensional structures in the continental crust and a new regimen of magmatic activity gave rise to the Cretaceous and Tertiary deposits. The deposits formed in the earlier cycle in a thin or poorly developed continental crust are associated either with syenite, monzonite, or fennite as at Stikeen and Copper Mountain or with quartz diorite and granodiorite as at Highland Valley. The later deposits that formed in a thicker continental crust are associated with quartz monzonite.

Breccia pipes are present in 20 of the 27 deposits considered by Lowell and Guilbert (1970), and wide zones of closely and irregularly fractured rock (crackle zones) surround almost all the deposits. This last feature is a very useful one in the recognition of porphyry deposits in the field.

Lowell and Guilbert (1970, p. 403–404) described the hydrothermal alteration of a typical deposit as forming in response to a "physical-geochemical continuum from low-temperature magmatic to 'conventional' hydrothermal conditions" in which hydrogen ion concentrations increase outward or with time. Where the country rock is homogeneous, a series of symmetrical, concentric shells of distinct hydrothermal mineral assemblages may be produced around the igneous intrusive. From the interior of the deposit outward, these are the potassic (quartz-K-feldspar-biotite), the phyllic (quartz-sericite-pyrite), the argillic (quartz-kaolin-chloride), and the propylitic (chlorite-epidote-carbonate-adularia and albite).

Many factors limit or disrupt the symmetry of the model porphyry copper deposit. Lowell and Guilbert listed (1) a strong regional structural fabric, (2) heterogeneity of preore host rocks, (3) postore faulting and intrusion, and (4) different levels of erosion exposing the deposits.

Titley (1972) drew attention to the profound effect of the country rock on the alteration mineralogy and on the form of the ore bodies. He distinguished "intrusion porphyry copper deposits" in which the ore body is mostly within the intrusive porphyry, from "wall rock porphyry copper deposits" in which the wallrock near a porphyry intrusion is altered and mineralized. Composites of these types are common. Titley emphasized that ore bodies in wallrocks may be just as valuable as those in intrusions and should not be overlooked because their alteration pattern does not follow the ideal model.

Porphyry copper deposits of the Pacific and Caribbean islands exhibit alteration patterns that diverge sharply from the Lowell and Guilbert model. Biotite is the most common mineral in the potassic alteration facies, and K-feldspar is commonly lacking, possibly because of the low availability of potassium in the intrusive quartz diorite and diorite porphyries and surrounding andesitic volcanic rocks. Propylitic alteration is widespread in these deposits, and in Puerto Rico it appears to follow an early period of biotitic alteration (Cox, 1971).

Figure 22 shows the size and grade characteristics of various porphyry copper deposits. The Bingham deposit in Utah is the largest in the United States, with a production since 1904 of over 14 million tons of copper (Anaconda Copper Corp., annual reports). The field of 22 U.S. deposits in production in 1960 has its center point at about 100 million tons at 0.8 percent copper or about 800,000 tons of copper metal per deposit.

A second field of eight U.S. and Canadian deposits brought into production in the last 10 years shows a downward trend in grade. At Sierrita, Ariz., the mining of ore averaging 0.34 percent copper is made possible by lower cost mining and processing methods. These new deposits contain on the average about 2 million tons of copper each. Likewise, porphyry deposits with byproduct molybdenum discovered in other parts of the world are being brought into production at average copper grades as low as 0.18 percent (Brenda, British Columbia) and 0.3 percent (Casino, British Columbia) (Peters, 1970). La Caridad, Mexico (Peters, 1970) and the combined San Manuel–Kalamazoo deposits, Arizona (Peters, 1970; Thomas, 1966, p. 139) are the largest of the new deposits, with about 7 million tons of copper each.

Overshadowing these are the great Andean porphyry deposits of Chile and Peru. These deposits were brought into production with average grades of 1–2 percent, and the average of 11 deposits plotted is about 4 million tons of copper each. The El Teniente and Chuquicamata deposits in Chile, which would lie on the right side of this field in figure 22, are larger by at least an order of magnitude than the majority of North American porphyry deposits. It is obvious that the Andes represent a copper province of great wealth and that numerous other lower grade deposits await development.

The principal byproduct metals of porphyry deposits are molybdenum, gold, and silver. King (see "Molybdenum" chapter) gives a range of MoS_2 values of 0.015–0.1 percent for porphyry copper deposits; Simons and Prinz (see "Gold" chapter) give a range of 0.001–0.025 ounce gold per ton in copper deposits in general. An average silver value of 0.06 oz per ton is given for 14 Arizona porphyry deposits by Heyl and others (see "Silver" chapter). Kesler (1971) pointed out that continental porphyry deposits have higher molybdenum values and that island arc deposits have higher gold values and lower molybdenum values. Gold content of the Panguna deposit in Bougainville is 0.018 oz per ton; the Marcopper deposit in the Philippines contains 0.001 oz per ton (Espie, 1971; Loudon, 1972). Molybdenum values in these deposits are negligible.

Economically important trace amounts of selenium, tellurium, and rhenium are derived from copper and molybdenum concentrates from porphyry deposits. Pyrite concentrates are recovered for their use in sulfuric acid manufacture, and magnetite concentrates are recovered from some porphyry deposits such as Atlas in the Philippines (Madamba, 1972).

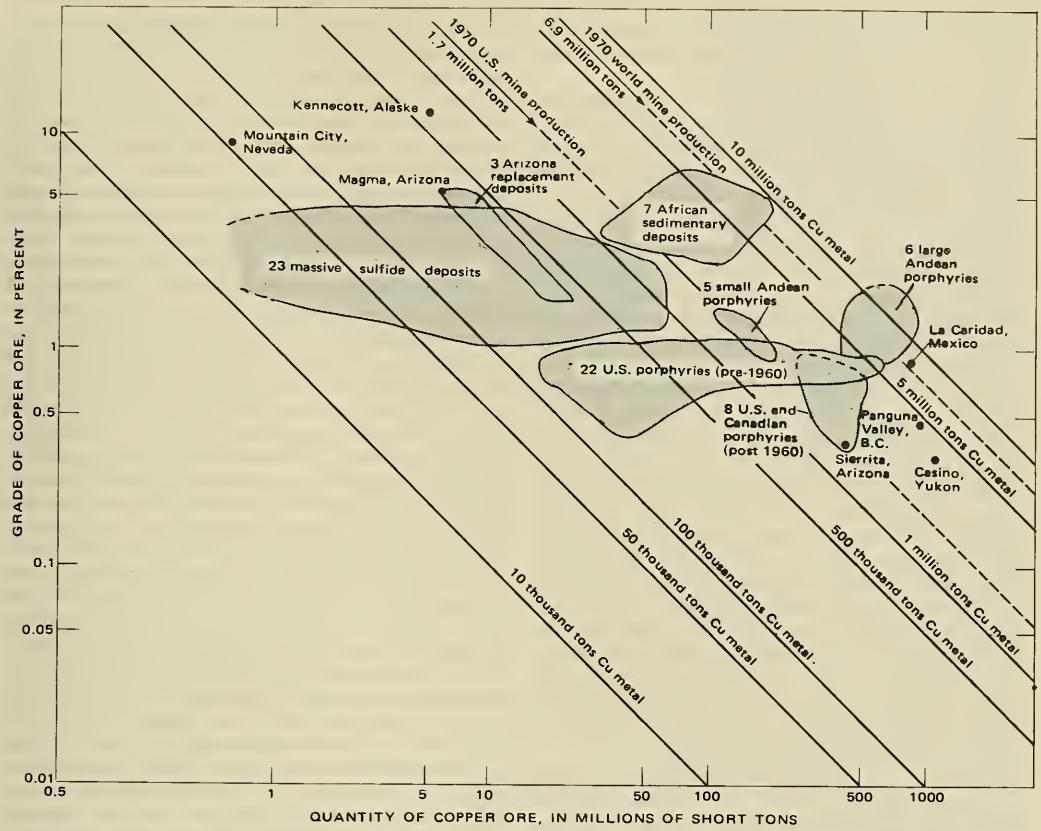

FIGURE 22.—Size and grade characteristics of selected copper ore bodies. Diagonal lines show tons of copper metal per deposit; world and U.S. mine production of copper metal are shown for comparison by diagonal dashed lines. Data from unpublished compilation by A. R. Kinkel, Jr., and others and from Peters (1970).

VEINS, PIPES, AND REPLACEMENT DEPOSITS

Copper-rich veins, pipes, and replacement deposits may be localized in felsic plutonic rocks with local porphyry intrusions as at Butte, Mont. (Meyer and others, 1968); in favorable host rocks near a porphyry copper deposit as at Bingham, Utah, and Bisbee, Ariz.; or near barren felsic intrusive rocks as at Magma, Ariz. (Hammer and Peterson, 1968) or Mission, Ariz. (Kinnison, 1966). Veins are formed when metal-rich solutions, emanating from a crystallizing intrusion, deposit minerals in faults or fractures. They are tabular in form and may show mineral textures indicating growth of crystals in open cavities as well as replacement of wallrocks by copper minerals. Many veins show several generations of mineral deposition related to opening and reopening of fault zones by tectonic movements.

Hydrothermal alteration envelopes may accompany the veins, indicating chemical reaction between wallrocks and mineral-rich solutions. Sales and Meyer (1949), in their monumental study of quartz-sulfide veins at Butte, Mont., described a sequence of alteration zones outward from the veins into the quartz monzonite wallrocks. The sequence is consistently sericite to kaolin to montmorillonite to fresh wallrock. Comparison of the chemical composition of these zones suggests diffusion of some ions from the rock into the vein and simultaneous migration of hydrogen ions into the wallrocks. There

is a close similarity in mineralogy between large-scale alteration zones extending outward from porphyry deposits and small-scale alteration zones successively enveloping sulfide veins.

Ore pipes are rodlike in form as contrasted to tabular veins. They may form in fractured or brecciated rock at the intersections of faults or by explosive release of gases derived from intrusive magmas. These latter are called breccia pipes because of the broken rock associated with them. At many places copper deposits in breccia pipes show a close spatial and genetic relation to mineralized porphyry intrusions as at Cananea, Mexico (Velasco, 1966) or a close geographic relation to porphyry copper deposits as in the porphyry copper belt in Chile (Sillitoe and Sawkins, 1971).

Replacement deposits form in reactive host rocks near the intrusive contacts or along mineral veins. These hosts may be sedimentary rocks such as limestone, dolomite, or calcareous sandstone or even diabase sills as at Ray, Ariz. (Metz and Rose, 1966). Replacement deposits tend to be tabular in form and may be roughly concordant with bedding. Though high in grade at some mines, when these deposits are removed as part of a large low-grade ore body they are generally regarded as part of the porphyry copper ore body, as at the Mission and Pima mines in Arizona. Mining of porphyry ore at Bingham, Utah, encroaches steadily on chalcopyrite replacement bodies in limestone beds to the west, and the distinction between ore in porphyry and ore in wallrocks becomes academic.

Favorable host rocks for replacement deposits may have continuity over large areas, and the recognition of their stratigraphic position is of great importance in the search for new deposits. In Arizona, increasing attention is being paid to details of local stratigraphy in attempts to locate hidden replacement deposits (Eyde, 1972).

Vein, pipe, and replacement ores have a more varied mineralogy than the porphyry deposits. Chalcopyrite and bornite are the most common hypogene minerals. Chalcocite and covellite may be present as hypogene minerals in addition to forming secondary enrichment blankets. At Butte, Mont. (Meyer and others, 1968), main-stage mineralization gave rise to veins of four distinct types: veins of the deep-level chalcopyrite zone containing chalcopyrite, bornite, and tennantite; veins containing chalcocite-enargite in the central zone; bornite-chalcocite-chalcopyrite-enargite veins in the intermediate zone; and carbonate veins containing rhodochrosite, sphalerite, galena, and rhodonite in the peripheral zone.

At the Magma mine in Arizona (Hammer and Peterson, 1968) vein ores contain chalcopyrite, bornite, enargite, tennantite, chalcocite, digenite, and sphalerite. Enargite predominates in the lower levels and gives way upward to tennantite, but sphalerite predominates in the upper levels. Digenite is present only in the lower levels. In the limestone replacement ores, chalcopyrite is predominant.

Mineral zoning such as is exhibited at Butte and Magma is present to some extent in most vein and replacement deposits. In addition to this a larger scale mineral zoning has been noted around most mineral deposits related to felsic intrusive rocks. Lowell and Guilbert (1970) in their tabulation of 27 porphyry copper deposits described some peripheral mineralization in all the deposits and arcuate clusters of small mines and prospects in 23 of the deposits. Most of these peripheral veins contain gold and silver values along with pyrite, chalcopyrite, sphalerite, specularite, enargite, famatinite, tetrahedrite, barite, and manganese and vanadium minerals. Recognition of a cluster of small veins as part of an outer zone surrounding a buried ore deposit may be an important step in the discovery of new copper resources.

Vein and replacement deposits are difficult to characterize in terms of tonnage and grade. If the Butte district is considered as one deposit—and no criteria seem to exist as a basis on which to subdivide it into smaller deposits—the amount of contained copper metal is enormous, rivaling that of the largest Andean porphyry deposits. In the period 1880 to 1964 the Butte mines produced more than 8 million tons of copper (Meyer and others, 1968). In Arizona, major vein and replacement deposits fall into a field (in fig. 22) with an average copper content of 350,000 tons of copper each.

In general, copper resources in vein, pipe, and replacement deposits are small in comparison to those of the closely related porphyry copper deposits, and discoveries of new deposits similar to Butte or Magma have declined sharply in the last few decades. The relatively small size of the ore bodies and alteration envelopes makes these deposits difficult targets in areas of deep overburden. It is likely, however, that vein, pipe, and replacement ore bodies will be discovered incidentally in the search for porphyry deposits.

STRATA-BOUND DEPOSITS IN SEDIMENTARY ROCKS

Strata-bound deposits in sedimentary rocks include some of the world's largest sources of copper. The sedimentary deposits of Zaïre and Zambia alone make up 15 percent (table 39) of the world's identified resources, and enormous deposits are known in

the U.S.S.R. Deposits of this type represent the largest potential for discovery of new deposits. Not only are many of them difficult to recognize in the field, but the geologic controls of their origin are only beginning to be understood.

A genetic classification of sedimentary copper deposits should distinguish ores formed by chemical or biological processes from those formed by mechanical processes; those deposited simultaneously with the enclosing sediment from those formed by later alteration; and those formed in a reducing environment from those formed in an oxidizing environment. However, these processes are not mutally exclusive, and the criteria for distinguishing them are frequently equivocal. Idealized descriptions of different types of sedimentary copper deposits presented below, followed by descriptions of several important deposits that may be combinations of types.

Type 1.—Rocks of intermediate Precambrian age formed when atmospheric oxygen began to become abundant and to mobilize copper that was previously stable. These deposits may include copper reworked or leached out of earlier disseminated deposits. The deposits of the African copper belt and those in the Belt Supergroup of western Montana may be of this type.

Type 2.—Syngenetic marine deposits formed on the sea floor by precipitation or adsorption on organic matter. These deposits should show a systematic relation to lithologic facies and may be characterized by lateral persistence within a bed or facies. Mineral textures are typical of sedimentary rocks and the deposits may contain other metals, such as uranium, vanadium, and silver, that could precipitate under similar conditions. The Kupferschiefer and equivalent formations in Europe may be of this type.

Type 3.—Deposits formed by reaction of connate brines or meteoric ground water with chemically reactive strata such as black shale, sandstone containing carbonaceous matter, or carbonate rock. As discussed by Lindgren (1911), such deposits probably form during compaction and lithification and are localized by variations in permeability, structure, and chemical reactivity of the host strata. The deposits may be nonpersistent and highly variable in size, shape, grade, and texture of the ore. Typical ore is more coarse grained than syngenetic ore and may include local replacement of original framework grains. The associated metals are the same as found in syngenetic deposits. Favorable host rocks include nonmarine arkosic sandstones. The "red-bed" copper deposits near Cuba, N. Mex., are an example of this kind of deposit. The other types of deposits have probably been modified to some degree by the processes that form this type of deposit.

THE KUPFERSCHIEFER

The Permian Kupferschiefer of Mansfeld, in the German Democratic Republic, is a thin-bedded bituminous marine marl or shale about 50 centimeters thick containing copper, lead, zinc, and silver in economic concentrations and many other metals in unusually large amounts (Richter-Bernburg, 1941; Wedepohl, 1964, 1971). The equivalent Zechstein shales of Lower Silesia in Poland contain economic concentrations of copper in some areas and of lead in other areas (Haranczyk, 1970). Many Europeans regard the mineralization of the Kupferschiefer and equivalent units as syngenetic because the mineralization is confined to a thin stratigraphic unit and its distribution is related to lithologic facies (Richter-Bernburg, 1951). Most advocates of the syngenetic hypothesis also suggest some extraordinary way of concentrating greater than usual amounts of copper from sea water. Submarine mineral springs and erosion of older copper ores are among the sources suggested for the copper. More recently, Brongersma-Sanders (1968) suggested that heavy metals could be concentrated in black shales and phosphorites by upwelling nutrient-rich waters. Davidson (1964) rejected all the arguments for unusual environments of deposition in favor of an epigenetic episode of mineralization by saline ground waters derived from the Zechstein salt deposits overlying the Kupferschiefer, citing as an example the metal-rich thermal ground waters encountered in wells near the Salton Sea as potential mineralizing solutions. Wedepohl (1971, p. 272) suggested a correlation between the local metal content of the Kupferschiefer and the soluble trace metals in the Lower Permian red sandstones over which the Kupferschiefer sea transgressed.

Much of the Kupferschiefer in West Germany is probably of submarginal grade, but there may be as much as several tens of millions of tons of rock with an average grade of 0.3 percent copper.

THE AFRICAN COPPER BELT

Nearly one-fifth of the world's production of copper comes from deposits in upper Precambrian sedimentary rocks that extend for about 300 miles across parts of Zambia and the Katanga province of Zaïre in Africa (U.S. Bur. Mines, 1970). These deposits are usually called "strata-bound copper deposits" because of some uncertainty as to their origin. Individual beds containing disseminated cop-

per sulfide minerals are persistent for many miles. The ore occurs in dark shales of the lower Roan Formation of the Katanga Supergroup. Most of the lower Roan Formation is made up of arkosic conglomerates and eolian sandstones overlying a granitic basement, but the dark shales of the main ore horizon also contain algal reefs. Thus, the ore horizon was probably deposited in a shallow restricted basin surrounded by algal reefs. An important feature suggestive of a syngenetic origin is the zonal arrangement of ore minerals within the ore formation parallel to the shoreline as it migrated back and forth with transgressions and regressions of the sea (Garlick, 1961, p. 155–160). The sequence proceeds from barren sediment along the shoreline through disseminated chalcocite, bornite, and chalcopyrite to pyrite in the same direction as the general flow of currents, as determined from crossbedding. However, the mineralized zone cuts stratigraphically upward through the succession from conglomerate to sandstone to argillite to impure dolomite.

The later discovery by Malan (1964) that chalcopyrite occurs in narrow argillaceous interstices between stromatolite columns in algal reefs is also cited as evidence that copper was deposited at the time of sediment deposition, perhaps by sulfate-reducing bacteria, or as a colloidal sulfate gel. Metal deposition in the copper, iron, and cobalt-bearing Chibuluma West ore body, Zambia, was syngenetic with sands and muds, according to Whyte and Green (1971) and could have been by (1) biogenic deposition of sulfides, (2) precipitation especially of iron and cobalt hydroxides by changes of pH where river waters entered the lake or branch of the sea, (3) detrital deposition of metalliferous minerals, or (4) by a combination of these methods. Many of the deposits in Zaïre have been altered by supergene enrichment, and they produce secondary copper minerals and a variety of other elements from dolomitic beds.

The very large resource of copper in the African copper belt may result from a combination of several important processes. If we assume that the deposits are syngenetic, they may have formed during the interval of Precambrian time when oxygen first became available in sufficient quantity to mobilize copper. Moreover, these deposits are at or near the base of a marine transgression which could mobilize copper in the underlying crystalline and nonmarine rocks in a manner suggested by Wedepohl (1971, p. 272) for the Kupferschiefer. Common features of the African copper belt and the Kupferschiefer were discussed by Putzer (1972).

The current rate of copper production from the African copper belt would suggest a known reserve of well over a billion tons of ore. Speculative resources may be several times as great.

PRECAMBRIAN SEDIMENTARY COPPER DEPOSITS IN THE UNITED STATES

At the White Pine district in Ontonogan County, Mich., copper occurs in the Nonesuch Shale of Precambrian Y age, especially in the basal parting shale bed (Ensign and others, 1968). About 5 percent of the U.S. copper production comes from this single bed which is 1–8 meters thick and contains anomalous copper over a distance of at least 250 kilometers (160 miles) in the Upper Peninsula of Michigan and northern Wisconsin. Chalcocite is the principal sulfide mineral in the mineralized zone whereas pyrite is the characteristic sulfide in the upper part of the Nonesuch Shale. The richest copper occurs in the darkest carbonaceous siltstones, shales, and sandstones, where chalcocite grains ranging in size from 2 to 20 microns are disseminated interstitial to the framework grains. Although the mineralization is persistent in certain beds throughout the district, a crosscutting relation between ore and bedding on a regional scale and the absence of a characteristic copper-bearing lithologic facies distinguish this deposit from the African copper belt. Consequently, an epigenetic, but not magmatic, source for the copper seems most likely. However, Robert Ehrlich and T. A. Vogel stated (oral presentation at Institute on Lake Superior Geology, Houghton, Mich., May 4, 1972) that according to their interpretation, the copper in the Nonesuch Shale is syngenetic, with some diagenetic modification of the distribution.

Strata-bound sedimentary copper deposits occur in Precambrian Y rocks of the Belt Supergroup in western Montana and adjacent parts of Idaho. Copper sulfides occur as disseminations, blebs, and veinlets in persistent beds of white fine-grained quartzite and siltite of the Revett Formation along a belt parallel to a broad domal feature formed before the close of Belt time. Anomalous amounts of copper are more widely known in green strata throughout the Belt basin. Most of the Belt rocks are feldspathic and contain variable amounts of mica (illite and sericite) plus chlorite in amounts inversely related to grain size. Anomalous amounts of silver and mercury are known to be associated with copper locally, but lead is known only in separate beds. The apparent relation between mineralization and a late Precambrian broad domal structure is suggestive of a diagenetic or early epigenetic

origin for the copper (Harrison, 1972). Later recrystallization and metamorphism to the biotite zone reduced rock permeability and precludes the possibility of late epigenetic mineralization.

Rocks of the Belt Supergroup, including the Revett Formation, may contain as much as 1 billion tons of ore with an average grade of 0.5–1.0 percent copper. Submarginal grade rocks with anomalous copper may be 10–100 times more abundant. Silver will be a valuable byproduct of the Belt ores when commercial exploitation begins.

PRECAMBRIAN SEDIMENTARY COPPER DEPOSITS IN THE U.S.S.R.

With an estimated reserve of at least 10 million tons of metallic copper (Sutulov, 1972, p. 10), the undeveloped sedimentary ores of Udokan in eastern Siberia (near 57° N., 117° E.) form one of the world's largest sedimentary copper deposits; Shank (1972, p. 88) reported that it may be the largest. The ores are mainly sedimentary and related to lithology, and the greatest ore concentrations occur in the 1,800–2,500-meter-thick Sakukan Formation within the 10,000–12,000 m Udokan Group of fine sandstone and siltstone and some thin lenses of carbonate (Bakun and others, 1958). The main layer within which ore masses occur is about 300 m thick, its top 250 m below the top of the Sakukan Formation. The top of a lesser ore-bearing layer is 1,250–1,950 m stratigraphically beneath the main one. Despite the great thickness of the Udokan Series, deposition was in shallow water, or in a littoral and deltaic environment.

The Udokan Series is considered by most geologists to be of Precambrian X age, but some geologists think it as young as Precambrian Z. Copper minerals were deposited with the sedimentary material or were diagenetic (Bogdanov, 1968). The copper is believed to have come from a Precambrian W shield area located to the northeast, containing anomalous quantities of copper. Part is believed to have been transported as fine clastic particles.

The Udokan Series is folded into a big synclinal basin, irregularly oval in plan; the southwest limb is overturned, but folding is not complex. The entire series is slightly metamorphosed, and some of the rocks are now quartzites and phyllites.

The main ores are disseminated chalcocite and bornite; there are also some chalcopyrite ores that are not associated with the preceding. Malachite, brochantite, and other secondary minerals are present in a restricted oxidized zone. Sphalerite, native silver, and molybdenite are rare in the deposit. Ore has been traced to depths of more than 1,500 m.

Lyubimov (1966, p. 231) described the remote location and problems that face development in the Udokan Series. The region has severe climate, permafrost, and seismicity and an elevation of more than 1,000 m above sea level, but the high metal content of the ore and the possibility of open-pit mining probably will compensate for the high capital expenditures needed.

RED-BED COPPER DEPOSITS

Numerous deposits of copper are associated with red sandstone strata of late Paleozoic or early Mesozoic age, as described by Lindgren (1911). In the Southwestern United States, only a few of the deposits are large enough to be mined economically. Host rock strata, interbedded with red strata, are generally light gray to dark gray and may weather yellowish gray. Nonmarine feldspathic or arkosic sandstones containing carbonaceous matter are the most common host rocks. Such copper deposits are similar in size and shape to some of the well-known deposits of uranium and vanadium in sandstone, and transitional deposits containing all three metals exist. The copper deposits generally contain some silver, and at Silver Reef, Utah, silver values exceed those for copper.

Near Cuba, N. Mex., the Nacimiento copper deposit, which occurs in the Agua Zarca Sandstone Member of the Chinle Formation, is a typical large red-bed copper deposit (Kaufman and others, 1972). Rich ore occurs as chalcocite, bornite, covellite, and secondary copper minerals, replacing fossil wood and forming halos around the wood. The deposit is clearly epigenetic, but appears to predate the major structural features of the area. In past years selective mining of rich chalcocite replacements of logs left much disseminated ore in the ground. The remaining disseminated and rich copper ore may be as much as several million tons in this area alone. The total speculative resources of copper in red-bed copper deposits of the United States may be several hundreds of millions of tons of mineralized material.

A second type of copper deposit generally included with red-bed copper deposits is represented by disseminated copper sulfide minerals currently mined from thin beds of gray shale in the Flowerpot Shale of Permian age in southern Kansas and western Oklahoma (Ham and Johnson, 1963; Johnson and Ham, 1972). The copper-bearing shales occur in a sequence that includes red sandstone, dolomite, gypsum, and shale and are facies equivalents of evaporite deposits including salt in western Kansas and in the Midland and Delaware basins of

Texas and New Mexico. Like the Kupferschiefer of Europe, these deposits have lateral persistence within thin strata, which is commonly cited as evidence for a syngenetic origin.

Strata-bound copper-bearing sandstones that occur in Carboniferous rocks of Dzhezkazgan in central Kazakhstan, U.S.S.R., are included here even though descriptions of these deposits indicate significant differences from our red-bed copper deposits. Copper sulfides with some lead occur in gray sandstone horizons interbedded with barren brown sandstones of shallow marine lagoonal and deltaic facies. As many as 27 zones of mineralized sandstone occur in 700 m of enclosing rock. The gray host rock is more calcareous and dolomitic than the associated barren rock. The primary ore consists of sandstone impregnated with bornite, chalcocite, chalcopyrite, and galena concordant with the lamination of the sandstone. The first stage of mineralization is probably syngenetic or diagenetic with the enclosing strata; it is cut by a second, epigenetic stage of copper-lead-zinc mineralization that forms intersecting veins, stockwork zones, and hydrothermal wallrock alteration. The ore-forming solutions may have been derived from basaltic magma at depth below the sea floor according to Shcherba (1971). These deposits were estimated to have a reserve of more than 3.5 million tons copper metal in ore containing 1.6 percent copper (Sutulov, 1967, p. 113).

MODERN SEA FLOOR NODULES

Extensive deposits of ferromanganese nodules now forming on the deep-sea floor in the major oceanic basins are examples of syngenetic copper-bearing deposits that may become economic in the near future as technology progresses. Although the origin and mode of concentration of metals in these nodules are the subject of intense debate, there can be no question that the nodules represent syngenetic deposition. The copper content of the nodules varies regionally in the ocean basins; the higher concentrations are normally on the west sides of the basins and between lats 10° N. and 10° S., 2,500–6,000 m below the surface. The nodules in the richer areas contain more than 25 percent manganese, as much as about 1.5 percent copper and nickel, and 0.25 percent cobalt, as well as many other elements in smaller quantity. The copper ions are thought to be adsorbed on the manganese oxides; copper minerals have not been reported. These nodules are discussd in more detail in "Manganese"; Mero (1965) reported information as to distribution and quantity.

METAL-RICH SEDIMENTS OF THE RED SEA

In March 1964, during an oceanographic survey of the Red Sea, scientists aboard the RRS *Discovery* found hot brine in the Discovery Deep. Subsequent exploration has shown that underlying the hot brine are iron-rich, brine-saturated sediments at least 10 m thick containing anomalous amounts of copper and zinc. The geology, chemistry, and physical properties of these sediments are discussed in detail in a collection of reports edited by Degens and Ross (1969). Aside from the economic potential of these deposits (Bischoff and Manheim (1969) estimated 50 million tons of brine-free sediment averaging 1.3 percent copper), the greatest interest lies in the theoretical implications of these deposits with respect to the origin of sedimentary deposits elsewhere. James (1969) suggested that deep burial of deposits of this type and continued circulation of hot brine through them would result in re-solution of the base metals and lateral migration. He speculated that such migration would continue until the solutions reached the H_2S-bearing reef limestones known to be laterally continuous with the metal-rich sediments, there to precipitate as sulfide minerals. Such a model provides a basis for new appraisals of the theories of origin of many types of sedimentary base-metal deposits. Furthermore, since the hot brines which have introduced the metals to the sea floor appear to be related to continental rifting, a tectonic control for sedimentary deposits is suggested. If stratigraphic and paleotectonic studies of a region suggest rifting and deep basin filling, favorable host rocks along the flanks of the rift may contain deposits of base-metal sulfides.

HORIZONTAL TRANSPORT OF SECONDARY COPPER DEPOSITS

A few localities are known where copper dissolved from sulfide-bearing rock as a part of the conventional surficial leaching has then traveled laterally and been deposited in a secondary zone that is not located above the primary sulfide. Perhaps this phenomenon is more common that is suspected, and consideration might be given to searching for such ores in the vicinity of subeconomic sulfide mineralization.

Lateral transport and secondary deposition of copper has been described at the Emerald Isle mine, Wallapai mining district, Arizona (Dings, 1951, p. 149–153), Jerome, Ariz. (Lindgren, 1926, p. 90–91), Chuquicamata, Chile (Newberg, 1967), Globe-Miami district, Arizona (Throop and Buseck, 1971), and Ray, Ariz. (Phillips and others, 1971). The transport distance at Chuquicamata was about 4

kilometers. Most of the deposits are in Quaternary gravels, but some are in older rocks.

MOBILIZED DEPOSITS OF PROBABLY SEDIMENTARY ORIGIN

Two major deposits, Aitik in northern Sweden and Mount Isa in Queensland, Australia, contain copper ores that were probably sedimentary in origin but have been modified by metamorphism. The ores of the old White Pine mine, Michigan, were deposited by hydrothermal solutions, but the source of the metal was probably the nearby strata-bound copper present in the Nonesuch Shale, the ore of the present mine. Many other deposits may also fall into this general category, and classification is harder as modification has increased.

The large low-grade copper deposit of Aitik, near Gällivare, Sweden, is in Precambrian gneisses, schists, and quartzites (Zweifel, 1972). The copper is in chalcopyrite and occurs with pyrite, magnetite, and pyrrhotite, mainly as disseminations and stringers. There was some hydrothermal alteration along with the mobilization of the sulfides.

At Mount Isa, lead-zinc-silver ores form masses that are conformable with the bedding of the Precambrian Mount Isa Shale, but the generally associated copper ores are in shears, particularly where silica and dolomite have been introduced. Thus, the lead-zinc-silver ores are reasonably interpreted as syngenetic, but the origin of the copper sulfide ores is less certain.

ENVIRONMENTS OF DEPOSITION

An understanding of the origin and environment of deposition of sedimentary copper deposits has practical application in the search for new or hidden ore deposits. A search conducted in depositional environments comparable to those of known copper deposits should have a far greater chance for success than a random search. Environments worth consideration include depositional environments where syngenetic concentrations are optimum, as well as postdepositional environments where diagenetic or epigenetic concentration seem most likely, as follows:

1. Deep marine basin sediments associated with midocean ridges or continental plate boundaries, such as the recent sediments along the crest of the East Pacific rise and sediments in association with the hot brine pools of the Red Sea.
2. Continental-margin marine black shales associated with phosphorites, such as the Meade Peak Phosphatic Shale Member of the Phosphoria Formation of Permian age in western Wyoming.
3. Shallow marine or estuarine shale associated with evaporites or nonmarine deposits, such as the Flowerpot Shale of Permian age in Oklahoma and the Kupferschiefer of Permian age in Germany and the equivalent Zechstein beds in Poland.
4. Sandstone, shale, and carbonate rocks exposed to migrating saline ground waters, such as alkaline carbonated waters or chloride brines derived from subsurface solution of evaporites. Examples might be the "Speckled Sandstone" of probable Early Permian age in the Salt Range of Pakistan, the Flowerpot Shale of Permian age in Oklahoma, the Santa Rosa Sandstone of Triassic age in New Mexico, and the San Andres Limestone of Permian age in New Mexico.
5. First-cycle sedimentary rocks in a restricted or closed basin, such as the Agua Zarca Sandstone Member of the Chinle Formation of Triassic age along the west flank of the Nacimiento Range, N. Mex.
6. Pyritic shale associated with submarine volcanism, as perhaps the Nonesuch Shale of Precambrian Y age in Michigan and Wisconsin.
7. Pyroclastic or porous carbonate-bearing rocks exposed to ground water from weathering copper-sulfide deposits, like the Apache Leap Tuff of Miocene age at the Inspiration mine, Arizona (Throop and Busek, 1971).
8. Stratified rocks of mostly Precambrian Y age (800–1,600 million years), especially if they are first-cycle sediments deposited in shallow-water or restricted basin environments. Examples are the Revett Formation of the Belt Supergroup in northwestern Montana, and the Roan Formation of the Katanga Supergroup in the African copper belt.
9. Basal transgressive marine rocks directly overlying deeply weathered crystalline rocks or first-cycle arkosic clastic strata, such as the Kupferschiefer of Permian age in central Europe and the Roan Formation of Precambrian age in the African copper belt.
10. Porous strata updip and marginal to deeply buried volcanic rocks of basaltic to intermediate composition, as the amygdaloidal flow tops and conglomerate beds of the Portage Lake Volcanics and perhaps also the Nonesuch Shale, both of Precambrian Y age in the Upper Peninsula of Michigan.

11. Porous or chemically reactive strata, including lava flows and pyroclastic rocks, within or peripheral to rocks of the zeolite facies of low-grade metamorphism. Examples besides the Nonesuch Shale are the Sangre de Cristo Formation of Pennsylvanian and Permian age in southern Colorado and the Apache Leap Tuff at the Inspiration mine, Arizona.

The environments described above are not all mutually exclusive; therefore, a coincidence of several may greatly increase the probability of finding significant copper mineralization.

SIZE AND GRADE CHARACTERISTICS

Sedimentary deposits are difficult to characterize as to size. On the one hand, many separate mines are not in separate ore deposits but in parts of a continuously mineralized stratum, and on the other hand, very large tonnage figures have been mentioned for beds continuously mineralized over wide areas even though only a small part may be mined economically. In figure 22, a field of seven deposits in Zaïre and Zambia has an average copper content of 4 million tons each in ore averaging 3.5 percent copper. Totals of production and reserves for both the White Pine and Keweenaw Point districts in Michigan amount to 7 or 8 million tons of metal for each deposit but in lower grade ore. Estimates for the Udokan deposit in the U.S.S.R. exceed 10 million tons contained copper.

MASSIVE SULFIDE DEPOSITS IN VOLCANIC ROCKS

Copper is more abundant in basalt and andesite than in other igneous rocks. Under various conditions, this copper content may be concentrated to form an ore deposit of distinctly different form from those associated with felsic intrusions.

A small but locally important part of the world's copper resources is found in lavas and pyroclastic rocks laid down in the marine environment. These deposits are generally (1) stratiform or lenticular, and concordant with the bedding of the surrounding rocks, (2) of small lateral extent as compared to thickness, and (3) composed largely of sulfide minerals with small proportions of silicate gangue. Mineralogically the deposits consist mainly of pyrite and (or) pyrrhotite and varying amounts of chalcopyrite, sphalerite, and galena. The terms "massive sulfide," "cupriferous pyrite," or "massive pyrite" deposits have been used to identify this class.

The last decade has been extremely productive in theories of origin of massive sulfide deposits. Recognition of metamorphic features in the North American deposits by Kinkel (1962) and Kalliokoski (1965) permitted the interpretation that their emplacement was earlier than the events that deformed them. Regional geologic studies such as those of Goodwin (1965) in the Noranda area, Quebec, made possible the views that the deposits were a part of the volcanic rock complexes that enclosed them and not a later superimposed feature. Detailed studies of Kuroko-type ores in Miocene tuffs of Japan (for example, Horikoshi, 1969) showed that these ores were formed on the sea floor during the last stages of an eruptive cycle. The equivalence of these deposits to the metamorphosed massive sulfides of older terranes had by this time become clear to many workers.

Anderson (1969) presented a thorough review of the genesis of these deposits, and in 1970 the meeting of the International Mineralogical Association–International Association on the Genesis of Ore Deposits in Japan brought together an outstanding group of papers on the subject. The description which follows is largely taken from papers by Tatsumi and Watanabe (1971), Hutchinson and Searle (1971), and L. A. Clark (1971) in the proceedings of that meeting.

Massive sulfide deposits that are undeformed by later orogenic activity exhibit a wide variety of textures and forms. Ore may be found in disseminations and stockworks or swarms of veins in highly propylitized lava. Above these may be found sulfide ore in cavities between pillows as at Cyprus. Massive sulfide bodies above the stockworks and vein swarms may show banding and colloform texture indicating deposition in open cavities or on the open sea floor. The ore may be intensely brecciated with interfragmental spaces filled with fine-grained sandy pyrite, and evidence exists for gravitational transport of blocks of ore, lava, and soft bottom sediment downslope on the sea floor from the source of the deposit. Overlying the massive ore are bedded deposits rich in iron oxides, silica, and disseminated pyrite. These bedded deposits are thickest over the massive ore, and they thin abruptly laterally.

The preceding features have given rise to the volcanic exhalative theory of origin. Metal-bearing solutions or vapors are thought to ascend rapidly through fractures in a submarine volcanic pile and to precipitate, partly in colloidal form, in near-surface cavities and on the sea floor. Deposition of sulfides may temporarily seal the vent area, and the resulting increase of vapor pressure may cause the brecciation of previously deposited ore. Mixing of iron-rich solutions with oxygen-rich circulating

sea water results in deposition of the overlying bedded siliceous ironstones.

The source of metals for these deposits is the same magma that gives rise to the surrounding volcanic rocks. Different lava types give rise to deposits of different mineralogy. For example, pyrite-pyrrhotite-chalcopyrite deposits are commonly associated with mafic volcanics, and sphalerite- and galena-bearing deposits tend to be found with silicic volcanic rocks (Anderson, 1969).

Copper-bearing massive sulfide deposits contain as much as 10 percent copper, with a mean in commercial ores of about 2.5 percent, and they range in size from a few hundred thousand tons to more than 50 million tons. The wide range in production grade of copper is due in part to the variable content of zinc, lead, silver, and gold in these ores as well as the economics of recovery of sulfur and iron from them.

COPPER IN NICKEL ORES

Many of the commercial nickel deposits in mafic rocks throughout the world have copper associated with them, and this "byproduct copper" is an important contribution to the supply, especially in Canada and the U.S.S.R. These deposits are generally interpreted to have been formed by a magmatic-segregation process as a part of the intrusion of the bodies of mafic rock.

The chalcopyrite-pentlandite ores related to mafic intrusives range in composition from mostly copper sulfides to mostly nickel sulfides, depending on the composition of the primary magma; the proportion of nickel increases roughly with maficity (T. P. Thayer, oral commun., 1972). In certain cumulate mafic bodies this may result in high-nickel sulfide at the base and more cupreous sulfide in higher strata (Thayer, 1971, p. 242). In these ores the sulfide has generally separated as an immiscible liquid, and the richest concentrations in these sulfur-rich magmas formed when the sulfide separated before crystallization had gone very far. Many papers in Wilson (1969) deal with the origin of ores of this type.

The most significant producer of copper from nickel-bearing mafic rocks is the Sudbury district of Ontario. In this area of complex geology, the ores, some stratiform and some crosscutting, are polygenic in relation to their enclosing rocks but were probably all derived initially as products of crystallization and the separation of a sulfide-rich dense liquid. Variation in the Ni:Cu ratio in different ore bodies makes it possible for a mining company to adapt the ratio in the ore produced to metal-market conditions.

Besides the Sudbury district, nickel sulfide deposits containing appreciable quantities of copper are found as segregations in mafic intrusive bodies in Maine and New Brunswick, in Quebec, Manitoba, Saskatchewan, and particularly in the coastal crystalline belt of British Columbia and southeast Alaska. The copper-nickel ores of Norway, Sweden, Finland, and the Kola Peninsula, U.S.S.R., are mostly polygenic and complex. The nickel-copper-cobalt ores of Noril'sk in north-central Siberia are also an important source of copper for the U.S.S.R. Nickel ores in Precambrian ultramafic and mafic rocks in the newly discovered Kambalda district in Western Australia contain 0.25–0.57 percent copper.

The deposits in Minnesota are in the Precambrian Duluth Gabbro Complex in the northern part of the State. Disseminated copper and nickel sulfides form discontinuous lenses and layers in the basal part of the gabbro complex. Recent studies show that although these deposits are not minable under present conditions, they represent a very important future copper resource (P. K. Sims, oral commun., 1972).

NATIVE COPPER DEPOSITS OF THE KEWEENAW TYPE

On the Keweenaw Peninsula, Mich., deposits of native copper occur in amygdaloidal flow tops and conglomerate beds in the Portage Lake Volcanics. These strata-bound and in part conglomerate-bed-controlled ores are mostly interpreted to be epigenetic in origin and may have affinities to some strata-bound ores in sedimentary rocks. (Bateman (1950, p. 498) likened them to the sandstone ores of Corocoro, Bolivia.) The proximity in both space and time of ores in the Portage Lake rocks to the mineralized Nonesuch Shale, 350–6,000 feet (110–1,850 m) above, also suggests this affinity.

Opposing this reasoning are the widespread minor copper occurrences in basaltic rocks all over the world, suggesting that the copper was originally syngenetic but has been redistributed and concentrated to minable grades by later processes (Cornwall, 1956, p. 620).

More than 5 million tons of copper metal has been produced on the Keweenaw Peninsula since mining began in 1845, and although there is little activity in the district now, large ore reserves remain.

Most of the copper is the native metal and was introduced into vesicles, fractures, and interstitial pore spaces after deformation of the rocks. Moreover, the copper deposits fit into a pattern of low-grade regional metamorphic zoning of silicate min-

erals similar to the zeolite facies described by Coombs, Ellis, Fyfe, and Taylor (1959). The source of mineralizing solutions for the copper sulfide deposits in the Nonesuch Shale and the native copper deposits in the Portage Lake Volcanics may be essentially the same—namely, the 15,000–30,000 feet of flood basalts at depth in the Lake Superior Basin (Ensign and others, 1968, p. 486). The copper-bearing solutions, according to White (1968, p. 322), may represent water driven from the voids and interstices of flow tops as the lava flows were crushed and metamorphosed in the axial region of the Lake Superior syncline, downdip from the present deposits.

Other copper occurrences that resemble the Keweenaw type are the chalcocite-bearing Coppermine deposits in gently dipping basalt flows of Precambrian Y age in the Northwest Territories, Canada, and the native copper-cuprite-azurite-malachite ores in chloritized and epidotized mafic flows in the Catoctin Formation (Precambrian Z) of Maryland and Virginia. Chilean copper deposits in terrestrial volcanic rocks such as Buena Esperanza (Ruiz and others, 1971) may be similar in origin to the Keweenaw type, although they lack native copper. Bornite, chalcocite, and chalcopyrite are found in amygdaloidal upper parts of andesite flows in these deposits.

MISCELLANEOUS TYPES

Some copper deposits of local and (or) historic importance differ significantly in form and rock association from those of the five major groups just described. Among these are small and very high grade chalcocite deposits such as Kennecott, Alaska, and Mountain City, Nev. (See fig. 22 for comparison with other types.) Nearby volcanic rocks have been called upon as a source of copper in these deposits (Coats and Stephens, 1968; E. M. MacKevett, written commun., 1972). The massive chalcopyrite lenses and veins of Matahambre, Cuba, appear to be unrelated to either volcanic or intrusive rocks (R. A. Bradley, oral commun., 1972). The sulfide lenses in shears crosscutting anorthosite bodies at Chibougamau, Quebec, do not lend themselves to inclusion with any of the previously described types.

Replacement ore bodies in carbonate rocks far from an igneous source, such as at Bornite-Ruby Creek, Alaska (Runnels, 1969), may be an important resource of copper. Numerous lodes of this type in a 450-mile belt along the south slope of the Brooks Range, Alaska, are believed to contain more than 10 million tons of copper metal. Small copper production (12,000 tons in 1970) from Missouri is a byproduct of the lead-zinc replacement bodies in carbonate rocks without igneous affiliation (Allen Heyl, oral commun., 1972).

RESOURCES

IDENTIFIED AND HYPOTHETICAL RESOURCES

About 70 percent of the world's identified copper resources fall into four distinct geologic-geographic groups. These are, in decreasing importance, porphyry copper deposits of Chile and Peru, porphyry copper deposits of the Southwestern United States, sedimentary copper deposits of Zaïre and Zambia, and porphyry copper and sedimentary copper deposits of the U.S.S.R. Other important groups are the porphyry copper deposits in Oceania, in Mexico, and in western Canada and the porphyry copper and sedimentary copper deposits in southeastern and central Europe, respectively. Volcanogenic deposits and nickel-copper deposits in mafic intrusions, important as they may be to local economies, do not contribute significantly to the worldwide picture.

Identified copper resources, given in table 39, are

TABLE 39.—*Identified and hypothetical copper resources, in millions of short tons*

Area	Identified [1]	Hypothetical [2]
United States:		
Eastern	10	5
Western, except Alaska	64	75
Alaska	2	20
Canada	19	50
Mexico	18	20
Central America	1	6
Antilles	2	1
South America	80	50
Europe, excluding U.S.S.R.	25	20
Africa	53	50
U.S.S.R.	39	50
Middle East–south Asia	4	20
China	3	?
Oceania, including Japan	21	30
Australia	3	3
Total	344	400

[1] Identified resources: Specific, identified mineral deposits that may or may not be evaluated as to extent and grade and whose contained minerals may or may not be profitably recoverable with existing technology and economic conditions. Based on all categories of reserve figures plus estimates where no figures are available. Amounts are tentative and accuracy will be refined in subsequent publications.

[2] Hypothetical resources: Undiscovered mineral deposits, whether of recoverable or subeconomic grade, that are geologically predictable as existing in known districts. Based generally on identified resource figures times a factor assigned according to geologic favorability of the region, extent of geologic mapping, and exploration.

those for which a size estimate is available. All categories of reserve figures as well as estimates for deposits where no reserve figures are published have been combined to make up this identified resource. These figures should be regarded as tentative, and considerable refinement of their accuracy should be expected in subsequent publications. They are derived from unpublished resource compilations made by A. R. Kinkel and others in the early 1960's, with additions and subtractions based on new dis-

coveries and estimated mine production, respectively. Low-grade deposits are not included here but are discussed under "Subeconomic Resources" of this chapter.

Hypothetical resources given in table 39 are those that have not been found but whose existence is suspected, as in concealed parts of known mineral districts, in projections of incompletely explored mineral belts, and in areas near important isolated new discoveries that suggest the possibility of a future mining district. The largest hypothetical reserves are in the Western United States, South America, Africa, and the U.S.S.R., all areas of favorable geologic setting and much recent successful exploration.

Hypothetical resources in the Western United States comprise the concealed deposits under basin fill in the major porphyry copper regions, a possible new porphyry copper province in the Absaroka Range of Wyoming, and the great resources of sedimentary copper in the Belt Supergroup of Idaho and Montana. Alaskan hypothetical resources are based on favorable evaluation of porphyry deposits in eastern Alaska and of replacement deposits in carbonate rocks on the south slope of the Brooks Range. Canadian hypothetical resources are in British Columbia and Yukon Territory. South American resources are in the Andes of Chile, Peru, Ecuador, and Argentina, and the estimate is probably conservative. African hypothetical resources are in the copper belt region and in the Precambrian rocks of southwest Africa. U.S.S.R. hypothetical resources are large, and the estimate of 50 million tons may be conservative; the resources comprise undiscovered porphyry deposits in the Kazakhstan and Uzbekstan regions and copper-bearing sedimentary strata in several areas. Another area where future discovery of important copper porphyry deposits can be reasonably expected is in the central Iranian volcanic belt northwest from the known porphyry occurrences near Kerman through the area near Hamadan and Tabriz and then westward across northern Turkey. In this area some types of copper mineralization related to intrusions have been reported by Superceanu. (1971, p. 395). The areas of copper prospects in northeastern and east-central Iran that may have potential for large copper deposits are discussed under "Speculative Resources."

The identified resources in the United States, 76 million tons of copper metal, are enough to last the country 45 years at the constant-use rate of 1.7 million tons per year; the world identified resource of 344 million tons will last 50 years at the rate of 6.9 million tons per year. At the same use rates, hypothetical resources add 60 years supply to the United States and 58 years supply to the world.

SPECULATIVE RESOURCES

During the last decade many new mineral provinces and districts were discovered and developed. Important examples of these are the porphyry copper deposits of the Canadian cordillera, the Southwest Pacific, and Iran. These areas had previously received little attention, and deposits of the porphyry type were thought to be limited mostly to Southwestern North America and the Andes. Similarly, sedimentary copper deposits, previously considered as rather unique occurrences, have been discovered in the Western United States and in eastern U.S.S.R. The development of these new provinces has drastically increased the resources.

There is considerable likelihood of finding even more new copper provinces given the new knowledge of copper metallogeny and perhaps aided by the same combination of economic boom and high metal prices that existed in the last decade. Future discoveries of porphyry copper and sedimentary copper deposits are more likely to have a major impact on the world's copper resources, and these types will receive the greatest attention. Unfortunately, not enough is known of the stratigraphic and paleotectonic controls of sedimentary copper deposits to be able to point to many areas with potential resources of this type.

In the United States, the greatest likelihood of new discoveries lies in the Southwest. In Arizona, the search for new porphyry copper deposits has been concentrated in the southeastern part of the State because of the greater number of known deposits and because more is known about the geology, geophysics, and geochemistry. Most of the southwestern, western, and northwestern parts of the Basin and Range province has not been evaluated adequately in reconnaissance, much less in detaill. Adequate geologic maps exist for only a few widely separated areas. The reasons for this are many and include inaccessibility, restricted access to military bombing ranges and Indian reservations, and inhospitable climate. Nevertheless, from what is known, these are pristine exploration areas, and must be considered to contain many copper deposits. On the basis of a simple comparison with the concentration of copper deposits in southeastern Arizona, and generally favorable regional geology, an order of magnitude of 10^8 tons is estimated for these areas.

Elsewhere in the Western United States, the Mountain City copper deposit in Elko County, Nev.,

which yielded over 100,000 tons of copper in ore averaging nearly 10 percent, is believed to have been derived from the nearby metavolcanic rocks of the Nelson Formation of Late Mississippian age (Coats and Stephens 1968). Volcanic rocks of Mississippian to Permian age are widespread in northwestern Nevada, and these and nearby sedimentary rocks offer numerous prospecting targets for high-grade copper deposits (Hewitt, 1968).

Metal-rich brines in the Salton Sea area of southern California and the Boleo copper deposits in Pliocene rocks in Baja California, Mexico, suggest a prospecting area. Upper Tertiary to Holocene rocks and sediments in and along both sides of the Gulf of California rift zone and its northern projection in the Salton trough may have been or may be in the process of being mineralized by metal-rich solutions rising through this rift zone.

In the Appalachian Mountains, the possibility of finding large porphyry copper deposits of Paleozoic age is intriguing. Ore-bearing porphyries are believed to be emplaced only at relatively high levels in the crust, during the final or postorogenic stages of a tectonic cycle. Thus pre-Mesozoic fold belts contain few of these deposits, because erosion in these areas has progressed to the point where most of the upper part of the crust has been removed. Special conditions, however, such as the deep burial and preservation of rocks of an early tectonic cycle by geosynclinal deposits of a later cycle, may result in the preservation of some older porphyry-type deposits such as at Catheart Mountain in Maine and those of the U.S.S.R. in central Asia.

Guild (1971) and Sillitoe (1972) discussed the relationship between porphyry copper deposits and the boundaries of major crustal plates and concluded that many deposits are related to the process of magma generation along the subduction zone where one crustal plate slides beneath another. Porphyry copper deposits tend to occur along the concave side of arc-trench systems resulting from the process of subduction. Recognition of ancient crustal-plate boundaries of this type would enable us to outline episubduction regions where porphyry copper deposits might occur. The Piedmont Province of the Appalachian Mountains may be such a region. H. L. James ("The Metallogenic Concept," Presidential address. Soc. Economic Geologists, Nov. 13, 1970, unpub. rept.) pointed out that this province has an arrangement of ore-bearing zones suggesting and eastward-dipping subduction zone. If porphyry copper deposits still are preserved they would lie in the Piedmont near the present edge of the Coastal Plain. Copper, lead, and zinc have been noted in several old mines forming a trend extending 400 miles northeastward from central Georgia to the North Carolina-Virginia boundary. Within this trend, several low-grade disseminated copper-molybdenum occurrences have been explored by drilling programs in recent years. Porphyritic intrusive rock has been reported from only the Magruder mine area in Lincoln County, Ga., but geologic reports on the old gold mines and prospects are mostly sketchy and limited to descriptions of the veins and the closely associated rocks. Some of the mines and prospects are reported to have areas of abundant disseminated pyrite.

In southwestern Alaska and the Aleutian Islands, geologic conditions similar to those of the Southwest Pacific permit the possibility of discovery of porphyry copper deposits. Quartz diorite intrusions and wide areas of disseminated pyrite described on Amchitka Island (Powers and others, 1960, p. 539, 541) suggest that in at least one locality a favorable environment exists for porphyry copper prospecting. Projection of the porphyry copper provinces of British Columbia and Yukon Territory into central Alaska suggests that large resources might be found there.

In the Antilles, an extensive copper province is suggested by the occurrence of porphyry copper deposits in Puerto Rico. The Puerto Rican deposits were formed during a period of vulcanism and intrusion in the early Tertiary (Barabas, 1971) and are overlapped by middle and upper Tertiary coastal plain carbonate rocks. A small molybdenum prospect in an Eocene pluton in the Virgin Islands (Ratte, 1971) suggests an eastward extension of this mineral province. In the limestone Caribbees, lower Tertiary plutonic rocks are exposed on St. Martin and Antigua. Hydrothermally altered rocks in St. Martin, Guadeloupe, Martinique, and other islands suggest interesting drilling targets, some of which were being explored by private companies during 1971. It is possible that another million tons of copper might be discovered in these islands, but land-use conflicts between mining and tourism may make their recovery in the near future doubtful.

West of Puerto Rico the lower Tertiary mineral province is interrupted. Volcanic rocks and potentially productive intrusive bodies are absent in the lower Tertiary sequence of Santo Domingo. However in the Montagnes Noires of Haiti, the Blue Mountains of Jamaica, and the southern Oriente Province of Cuba, lower Tertiary volcanic rocks are present. Quartz-bearing intrusive rocks and alteration zones that may be present in these areas represent high-priority targets for porphyry copper

exploration.

In western Colombia, quartz diorite intrusions of probable middle Tertiary age in the Sierra Occidental (Irving, 1971) suggest a large region where porphyry deposits might be found. Recent geochemical investigations by U.S. Geological Survey and Colombian government geologists have revealed strong copper anomalies in one of these intrusions in the north end of the Sierra (E. M. Irving, oral commun., 1972).

In Panama, recently discovered porphyry copper deposits related to upper Tertiary volcanic rocks (Ferencic, 1970; Dengo and others, 1969) suggest a wide province with potential mineralization.

Economically important copper deposits are unknown in the Precambrian shields of South America, but the region is vast, nearly unpopulated, and difficult of access. In Brazil, the recent highway construction and westward pioneering movement and accompanying geologic and geochemical exploration may yield copper resources of great size. Not enough is known of the geology of this region to do more than speculate on the possibility of major sedimentary copper deposits of the Zaïre-Zambia type or smaller deposits of the Tsumeb type.

In western Europe and northwest Africa, porphyry copper deposits of late Paleozoic age may be preserved. These could be products of a Paleozoic subduction zone resulting from the collision of the European-African and the American crustal plates. Goosens (1971) suggested the possibility of porphyry copper occurrences in western Africa.

The Alborz Mountains of northern Iran, with numerous small copper occurrences, may be a long extension of the copper-molybdenum porphyry province in Soviet Armenia. The areas of volcanosedimentary complex northeast of the Dasht-e-Lut in eastern Iran and in the northern part of the Chagai District in Pakistan, both areas of some late volcanism, are favorable areas for the occurrence of very young (Pliocene-Pleistocene) porphyries. One untested porphyry at Saindak in the Chagai District was described (Schmidt, 1968), and one prospect in east-central Iran, that at Gazu, was described in a way suggesting a porphyrylike deposit (Bazin and Hübner, 1969, p. 107–108).

Mesozoic fold belts of the Soviet Far East probably contain large porphyry copper deposits. The Koryak Peninsula would be the logical beginning for the search for these because of the apparent continuity of cordilleran-type structures into this area. Younger deposits may occur along the Kurile-Kamchatka-Aleutian arc-trench system.

Recent discovery of porphyry copper deposits in the Philippines, Solomon Islands, and Borneo suggests that all the island arc areas in the Western Pacific, especially the Indonesian islands, might be potential prospecting ground.

A region of abundant felsic volcanic rocks in northeastern China and eastern Mongolia would seem to have potential for significant copper-porphyry and massive sulfide deposits. Other ranges besides the Ch'i-lien-shan, especially in northern Tsinghai Province, might contain significant massive sulfide copper deposits. There is also considerable potential for sedimentary copper deposits in many parts of this large country. We do not know enough about recent Chinese geologic literature to speculate on extensions of the environment of the copper porphyry of Chung-t'iao-shan in Shansi Province.

The Tasman geosynclinal belt in eastern Australia contains many copper occurrences and major deposits of the massive sulfide type. Late Paleozoic felsic intrusions in this belt may contain large resources of the porphyry copper type.

Table 40 summarizes our estimate of the amount of copper that might be contained in these untapped districts and provinces. The figures are at best a guess and may be in error by as much as 100 percent.

TABLE 40.—*Summary of speculative resources, in millions of tons, of copper* [1]

Basin and Range porphyry copper	100
Alaska porphyry copper	10
Other Western United States possibilities, Appalachian Mountains porphyry copper, and Antilles porphyry copper	10
Central America—Colombia porphyry copper	10
Brazilian shield sedimentary copper	50
Western Europe–northwest Africa porphyry copper	10
Middle East porphyry copper	10
U.S.S.R. Far East and Kurile-Kamchatka arc	100
China	(?)
Australia	10
Indonesia	10
Total	320

[1] Speculative resources: Undiscovered mineral deposits, whether of recoverable or subeconomic grade, that may exist in unknown districts or in unrecognized or unconventional form. Based mostly on estimates of geologic favorability and extent of geologic mapping.

SUBECONOMIC RESOURCES

Lowell (1970) estimated that in the upper mile of the earth's crust there are about 3×10^{15} tons of copper. The recoverable identified, hypothetical, and speculative ore deposits discussed in the previous section make up a small fraction of this amount. Another fraction, subeconomic resources, comprise bodies of mineralized rock containing copper in amounts considerably higher than crustal abun-

dance but lower than could be mined under present economic and technological conditions. Subeconomic resources may be either identified or hypothetical, but inasmuch as data on grade and tonnage of subeconomic deposits are rarely available, no distinction is made between these categories. Subeconomic speculative resources represent such a high degree of uncertainty that they cannot be given numerical values. The lower limit of copper content of deposits in the subeconomic category depends on one's personal expectations of revolutionary advances in mineral recovery and mining methods. Copper will ultimately be mined at lower grades than most other metals because recovery is facilitated by its tendency to occur as minute sulfide grains rather than in silicates. However, adverse effects on the environment and the magnitude of the labor and power requirements mitigate against the creation of huge open-pit mines in rocks containing only a few hundred parts per million of copper.

Table 41 gives some of the identified and hypothetical subeconomic resources that may become economically important in the future.

TABLE 41.—*Partial list of subeconomic (conditional) resources, in millions of tons, of copper* [1]

Locality	Type of deposit	Copper resources
Western United States	Porphyry copper	20
Do	Sedimentary	20?
Eastern United States	Sedimentary	11
Do	Copper-nickel	60
Sea floor	Nodules	50 (40–60)
Western Canada	Porphyry copper	20
South America, Andes	do	100
Africa	Sedimentary	60
Europe	do	50
Total		381

[1] Conditional resources: Specific, identified mineral deposits whose contained minerals are not profitably recoverable with existing technology and economic conditions.

In the United States, conditional resources in porphyry copper deposits are probably very large. Lowell (1970, p. 69) predicted that average grades in open-pit copper mines will decline to 0.25 percent by the year 2000. In-place leaching of deposits of even lower grade may soon become economical. In addition, some large deposits such as at Safford, Ariz., are too deep or too irregularly distributed to permit profitable mining at the present time but may become minable in the near future. An estimate of the hypothetical subeconomic resources in porphyry copper deposits averaging 0.25 percent copper requires some knowledge of the frequency of such deposits compared with deposits of minable grade. Moreover, to predict the increase in reserves of known deposits in response to a drop in average ore grades requires some knowledge of the rate at which copper content falls off with distance outward from boundaries of porphyry copper ore bodies. If the slope of the curve of copper plotted against distance outward is steep for most deposits, decreases in average grade will have little effect on reserves. Inasmuch as these data are not available, we are reduced to making the simple assumption that there are at least as many deposits averaging 0.1–0.4 percent as there are deposits of currently minable grade. The discovery and development of this additional 7–8 billion tons of material in the western porphyry copper provinces with average grades of about 0.25 percent would yield about 20 million tons of additional copper.

Large conditional resources in sedimentary copper deposits in the United States are difficult to evaluate. Geologically, sedimentary deposits pass from economic ores to subeconomic resources when the beds in which the copper minerals occur become too thin or become separated by thick beds of barren rock. Also, some beds may have engineering characteristics that make mining dangerous or expensive, or a steeply dipping copper-bearing bed may reach depths that are beyond the reach of present-day underground mining practice. Nevertheless, the copper in certain sedimentary deposits is known to be continuous at fairly constant grade for great distances.

The Nonesuch Shale at White Pine, Mich., is such a deposit. W. S. White (oral commun., 1972) estimated that 11 million tons of copper metal exists in currently subeconomic mineralized beds. The sedimentary copper deposits recently being explored in the Belt Supergroup of Montana and Idaho probably contain large conditional resources, but no information is yet available on their minable reserves.

The copper-nickel deposits in the Duluth Gabbro Complex in Minnesota represent a large conditional resource. P. K. Sims (oral commun., 1972) estimated that 14 billion tons of mineralized rock exists along the lower contact of the gabbro body. This material has a lower cutoff of 0.25 percent and an average grade of 0.58 percent combined copper nickel. Assuming a 3 to 1 copper-nickel ratio, these deposits contain slightly more than 60 million tons of copper metal. Some of this copper is disseminated in bodies as large as 100 million tons and may soon become amenable to mass-mining methods, according to Sims.

Summing up these large conditional resources (table 41) gives a total of 111 million tons of copper which may at some time become available in the United States.

Among the world's most important conditional resources are those of the sea floor. These comprise

copper-bearing manganese nodules of the ocean basins and brine-associated metal-rich bottom sediments of the Red Sea. On the basis of Mero's (1965) estimates of copper content and abundance of ocean floor manganese nodules (see also "Manganese"), we estimate that 40–60 million tons of copper may be available from this source. Development of these resources depends on the accurate determination of their size, research and development on economical mining and metallurgical methods, and settlement of the international-legal problems of ownership.

Elsewhere in the world, reasonable assumptions on which to base estimates of presumed resources become increasingly difficult to make. In the Andes, where porphyry copper deposits are large and are mined at much higher grade than those in the United States and Canada, there must exist very large subeconomic resources. The sedimentary deposits of Zaïre and Zambia probably also contain very large amounts of copper in thin or deeply buried beds. A doubling of the copper reserves of these areas is not difficult to imagine when modern low-cost mining methods are established and (or) world copper prices rise.

Wedepohl (1971) gave 30–100 million tons as the probable copper content of the Kupferschiefer in Germany. Economic deposits are largely depleted, and this resource lies in thin or deeply buried beds.

PROSPECTING TECHNIQUES

We must assume that most easy-to-find copper deposits in the populated regions of the world have now been discovered. For all except some remote areas, new discoveries are more difficult to make and indirect methods of prospecting are being used increasingly to find copper and other metals. From now on, our success in finding new and especially hidden deposits will greatly depend on our ability to develop new methods of detecting concealed ores.

Some prospecting techniques can be applied to a wide variety of ores, but others are only for specific targets. Geochemical reconnaissance is often the first step in prospecting and usually seeks several metals that may be dispersed from any kind of ore deposit. Stream sediment sampling, described by Hawkes and Webb (1962), is the most effective reconnaissance method in many terranes. Refinements of this method, such as improved statistical analysis of data and sampling of certain mineral species (for example, magnetite), have had some success. Detailed study of anomalous areas and outlining of drilling targets are usually accomplished by soil sampling and analysis. In tropical areas copper can be mostly leached from soils overlying the deposits, but Learned and Boissen (1972) showed that over porphyry copper deposits, traces of gold associated with chalcopyrite remain in the soil and that the deposit may be outlined by the gold anomaly over it. In glaciated regions, ore fragments in boulder trains have been studied in hope of tracing them to their source; sulfide fragments were followed for 50 km in the discovery of the Outokumpu ores of eastern Finland.

Rocks containing widely disseminated pyrite associated with copper porphyry deposits, in combination with other effects of hydrothermal alteration, weather in the desert environment to produce a large color anomaly, "distinguished by brownish to greenish coloration, bleaching and variegated iron staining" (Jerome, 1966, p. 82–83). In some localities large red-brown areas ("red thumbs") have developed near the ore bodies as at Bisbee, San Manuel, and Banner-Pima-Mission, all in Arizona. Recognition of the "red thumb" area from an aircraft played an important part in the exploration of the La Caridad deposit, Mexico. The areas of color anomaly may be hundreds of meters to several kilometers in size and might be recognizable on colored aerial photography (Schmidt, 1968, p. 60). They also form target areas large enough to be sought from instrumented satellites; tests of the detection of a porphyry ore body in a desert area are planned for the Earth Resources Technology Satellite A.

Preliminary experiments have been made to compare the spectral reflectance from trees in soil over a sulfide mineral deposit with reflectance from trees of the same species on nearby unmineralized soil (Canney, 1970). Early results of tests made on a disseminated copper-molybdenum deposit in Maine have been encouraging.

Geophysical methods of many types are suitable for copper prospecting, but they are much more specific for certain types of ore. Aeromagnetic surveys are used to outline bodies of mafic rocks which may contain massive sulfide or magmatic-segregation deposits or to indicate areas of weakly magnetic hydrothermal alteration or highly magnetic skarn mineralization associated with porphyry deposits. The use of geophysical methods in the search for copper porphyry deposits was discussed by Brant (1966) and Sumner (1970). The potassic alteration that accompanies porphyry copper deposits can, theoretically, be detectable by modern airborne gamma-radiation surveys (Moxham and others, 1965). Electromagnetic surveys by ground or air are used in outlining massive sulfide deposits; induced-potential surveys are effective in locating

porphyries and other types of rocks that contain disseminated sulfides. The use of geophysical methods in the search for massive sulfide ores is discussed by several authors in Morley (1970).

Recent developments in geochemistry and geophysics have made it possible to recover more information from diamond drilling than simply the geology and copper assays of the core. Cheaper and rapid analytical methods, principally in spectroscopy, have made it more feasible to analyze large numbers of samples for many elements. Slight variation in trace-element composition may be caused by metals dispersed outward from an ore body not intersected by the hole. Similarly, down-hole geophysical instruments of many types have been perfected, enabling the geologist to extend his knowledge many feet beyond the walls of the drill hole.

PROBLEMS FOR RESEARCH

Figure 22 shows the relationship between the size and grade of ore deposits and copper production. Annual U.S. production is about equivalent to a deposit the size of Sierrita in Arizona, and annual world production is about equal to a La Caridad deposit or an average Zaïre-Zambian sedimentary deposit. It is important to know if we are mining our copper deposits faster than we are finding them. During the last 10 years, U.S. mine production was about 13 million tons of copper (table 36). New porphyry copper deposits discovered and (or) brought into production during this 10-year period, listed by Peters (1970), will yield slightly more than 14 million tons of copper. Assuming that several million tons of copper is known in other, less important types of deposits and in some large but unannounced discoveries, it appears that, in the United States, exploration and development are ahead of production by a small margin. Worldwide exploration and development lead mine production by at least 28 percent, again using Peters' list of discoveries.

The last decade was notable for intense exploration activity in response to favorable political conditions and high copper prices. Moreover, economic geologists experienced a renaissance in geologic theory during this period, in which new approaches to problems of geochemistry, igneous and sedimentary petrology, and tectonics were found and applied to ore deposits. However exploration geology is very sensitive to economic cycles, and there is reason to believe that this period of activity is over, at least temporarily (Colen, 1972). This stop-and-start exploration activity is extremely wasteful of human energy, and if we are to satisfy the long-term demand for metal in a future world in which ore deposits become increasingly more difficult to find, new ways of organizing exploration activities must be sought, especially long-range planning.

Copper is a commodity for which a permanent worldwide shortage is not easily foreseeable, but even though the hypothetical and speculative resources may be very large, an enormous amount of geologic field work, analysis, and even intuition will be required to transform these resources into proven reserves. At the same time we must continue to develop our scientific knowledge in order to replace outdated exploration ideas with new ones.

On the geological side of resource study, the need for geologic and geophysical maps as a base for mineral exploration cannot be overemphasized. More specifically, additional efforts must be applied to mapping and other geologic studies of those parts of the United States that have the highest mineral potential. Southeastern Arizona is probably the richest copper province in the world, yet geologic mapping at a scale of 1:62,500 is complete for only 27 percent of the area, and nearly half the province is unmapped.

Large-scale metallogenic maps might be an effective exploration tool in southeastern Arizona to detect the presence of deposits concealed beneath younger volcanic and sedimentary rocks.

Lowell and Guilbert (1970) and others pointed out that almost all porphyry copper deposits have a peripheral zone of small veins of base and precious metals, manganese carbonates, and barite that may extend outward for several miles from the deposit. Careful mapping of these veins, including even the smallest mineral occurrences, and careful classification of them according to various mineralogic, structural, textural, and genetic schemes may direct the exploration geologist to blind porphyry ore bodies or to those covered by later deposits. This mapping should be done at scales of 1:125,000 or greater depending on the complexity of the geology and spacing of the data points. Trace-element analyses of the veins and of mineral separates from them such as biotite or chlorite may aid in the interpretation. Studies of salinity and temperature of formation of fluid inclusions in the vein materials may show the geologist the direction toward the source of the mineralizing solutions.

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DIATOMITE

By David L. Durham

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ABSTRACT OF CONCLUSIONS

Diatomite is a rock made of microscopic porous shells of silica. Its principal domestic use is as a filtering material, for purifying water and various food processing and industrial fluids; other diverse uses include fillers, construction and insulating materials, and mild abrasives. United States and world resources of crude diatomite are adequate for the foreseeable future, but the need for diatomite near markets and for particular purposes encourages development of new sources for the material. Studies that relate the geologic setting and history of diatomite to the occurrence and properties of the rock can help locate important undeveloped deposits.

INTRODUCTION

Diatomite is a sedimentary rock composed mainly of the siliceous remains of diatoms, which are single-celled aquatic organisms that generally are classed as algae. Diatoms depend upon a form of photosynthesis; consequently they flourish only in sunlit waters. They develop frustules, or shells, of amorphous opaline silica ($SiO_2 \cdot nH_2O$) that commonly are complexly perforated and bear ribs, spines, and bristles; the combined area of holes in the frustules generally ranges from 10–30 percent of the total area (Lewin and Guillard, 1963, p. 378). Many valuable properties of the rock depend upon the aggregate effect of the microscopically complex and chemically inert diatom frustules. Papers by Conger (1951), Lewin and Guillard (1963), Lohman (1960), and Patrick and Reimer (1966) include much general information about diatoms.

Although the opaline silica of dead diatoms is soluble in most natural waters, the rate of solution is slow enough that siliceous diatom remains can accumulate under favorable conditions to form the substance of diatomaceous sediments and rocks. Rock composed almost entirely of diatom frustules generally is called diatomite; the term implies material of commercial quality. Although unconsolidated diatomaceous sediments are not properly classified by the rock name "diatomite", both the rock and the sediments are considered together as a commodity because they both are sources of diatom products. The names "diatomaceous mudstone", "diatomaceous siltstone", and "diatomaceous shale" describe rocks that contain diatom remains along with a considerable amount of other sedimentary material; these rocks are of less commercial interest than the more nearly pure diatomite. The names "diatomaceous earth" and "kieselguhr" are synonymous with the term "diatomite"; the names "moler" and "moler earth" apply to impure diatomite produced in Denmark. The names "infusorial earth" and "tripoli" are used improperly for diatomite. Numerous trade names identify the diatomite products of particular manufacturing companies. Papers by Calvert (1966), Conger (1942), and Lisitsyn (1967) describe the accumulation of diatomaceous sediments; papers by Cummins (1960), Eardley-Wilmot (1928), and Williamson (1966), and an article in Industrial Minerals (1969) summarize data on diatomite.

The most conspicuous features of diatomite are the light weight, high porosity, and whiteness of the material. Scanning electron microscope photographs of diatomite show plainly the fine aggregate structure responsible for many remarkable properties of the rock (Gillott, 1969, p. 104). Dry blocks of crude diatomite have an apparent density of 20–40 pounds per cubic foot, only about half that of water, although the specific gravity of the opaline silica of diatom frustules is about twice that of water. Dry diatomite powder has an apparent density of only 5–16 pounds per cubic foot. Diatomite is highly porous, and the porosity increases with increasing temperature up to about 700°C. It has low thermal conductivity and the melting point ranges from about 1,400° to 1,750°C; certain impurities lower the melting point considerably. The rock can absorb 1½–3 times its weight of water; the absorptive capacity is increased when the combined water of the opaline silica is driven off by calcination. Diatom products also have useful adsorptive properties (Anderson and others, 1947). Diatomite has a dull earthy luster and generally is white or nearly white, although both impurities and water content affect the color. Diatomite ranges from massive to finely laminated and, ordinarily, it is easily friable. The opaline silica of diatoms has a hardness of 4–6 on the Mohs scale, but the rock itself has an apparent hardness of only 1.5

Chemical analyses of diatomite generally show 70–90 percent SiO_2, 2–10 percent Al_2O_3, and variable but small percentages of Fe_2O_3, FeO, TiO_2, P_2O_5, CaO, MgO, Na_2O, and K_2O (Cressman, 1962, table 3; Cummins, 1960, table 1).

The physical properties of diatomite vary considerably from one deposit to another and may vary from bed to bed in a single deposit. The varieties and commercial grades of diatomite depend mainly on (1) the kind and amount of impurities in the crude material, and (2) the aggregate effect of the shape, size, arrangement, and relative proportions of the constituent diatoms. The commercial value of diatomite generally is affected adversely by impurities such as clay, volcanic ash, sand, carbonate, and organic matter. Also, the commercial quality of the material is lessened if the constituent diatom frustules are crushed or broken.

USES

Diatomite has hundreds of specific uses in 10 principal categories: (1) filters, (2) fillers (see "Pigments and Fillers"), (3) insulating materials, (4) mild abrasives, (5) absorbents, (6) catalyst carriers, (7) reactive-silica source, (8) structural materials (see "Lightweight Aggregates"), (9) additive or pozzolan for concrete, and (10) conditioner or anticaking agent. The first category, filters, accounts for more than half of the diatomite consumed in the United States—58 percent in 1969 (West, 1971, table 2). Processed diatomite is an especially effective filter aid, or fine powder, that is mixed with a liquid to be filtered; the filter aid forms a continuously building porous cake on the filter medium and retards clogging of the filter pores by trapping impurities. The suitability of diatomite for filtration depends largely on the shapes and sizes of the constituent diatoms. Diatomite that contains a substantial percentage of long hairlike diatoms together with fragments of discoid diatoms generally is best for retention of fine impurities while allowing a high rate of flow; rock of this type is mainly of marine origin. Diatomite has a role in the purification and clarification of a host of chemicals, beverages, foods, pharmaceuticals, and other liquids. Its use in water purification expanded greatly following development of diatomite filters for military use during World War II.

The chemical inertness of diatomite (readily soluble only in hydrofluoric acid and strongly alkaline solutions) makes the material especially useful as a filler, extender, or diluent in many products, including paints, papers, insecticides, plastics, and fertilizers. This second category of uses accounts for about 20 percent of the diatomite consumed in the United States (West, 1971, table 2).

PRODUCTION

The United States leads the world in diatomite production—followed by the U.S.S.R., Denmark, France, West Germany, and Italy—and is the dominant producer of filtration-quality material (West, 1971). Both the United States and world production increased during the 20-year period 1949–68 (fig. 23). The United States exports substantial amounts of prepared diatomite—176,000 short tons in 1969, valued at $13,510,000 (West, 1971, table 4)—mainly filtration-grade material. Although transportation is a major factor in the cost of diatomite products, high-quality filter-aid material is exported regularly from the Western United States to European and other distant markets. United States imports of diatomite are small—47 short tons in 1969 (West, 1971, p. 484).

GEOLOGIC ENVIRONMENT

Diatoms are one of the chief agents by which silica is removed from solution in marine and fresh waters; their role as consumers of dissolved silica

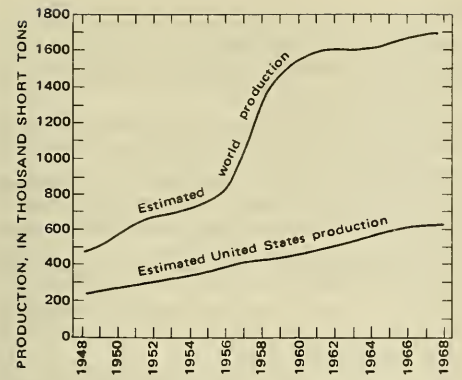

FIGURE 23.—Estimated diatomite production, 1948–68, adapted from production figures and estimates by the U.S. Bureau of Mines (1958–71). The pronounced upturn in the world production curve between 1956 and 1960 mainly reflects increased production figures for Denmark and France and larger production estimates for the U.S.S.R.

and the concentration of biogenous silica in their accumulated remains are major factors in the silica balance of most water bodies. Diatoms live in nearly all aquatic environments, but they form thick pure deposits only where they flourish for a considerable time away from contaminating sediment sources. Preservation of the siliceous parts of diatoms may be favored in sediments high in organic matter (Berger, 1970, p. 1387); also, the inclusion of diatoms in fecal pellets may enhance the chance of preservation of diatom frustules because the membrane that encases a pellet protects the frustules from dissolution, and the pellets speed the fall of frustules through the water column (Schrader, 1971, p. 56–57).

Because diatoms growing in abundance soon deplete the silica supply of near-surface water, sustained diatom production depends on continued renewal of silica-rich water to the surface. The interaction of many factors determines the abundance of diatoms at any particular place and time, but commonly diatoms proliferate in marine areas of upwelling, in lakes on volcanic terranes, and in lakes in areas that had Quaternary glaciers. Although marine diatomite commonly is associated with volcanic rocks (Bramlette, 1946, p. 39; Khvorova, 1968, p. 111; Taliaferro, 1933, p. 36), at some places oceanic circulation alone supplies sufficient silica to account for thick accumulations of diatomaceous sediments without requiring introduction of additional silica from nearby volcanism (Calvert, 1966, p. 593). The beneficial effects of an ash fall on the diatom population of a modern lake have been shown (Kurenkov, 1966, p. 429), but silica seldom is a limiting factor in diatom production in lakes except during intensive diatom blooms (Schelske and Stoermer, 1971, p. 423). Papers by Gregor (1968), Grill (1970), Harriss (1966), Krauskopf (1956), and Siever (1957) consider the role of biogenic silica in maintaining the silica concentration of natural waters.

Marine diatoms occur in rocks as old as Mesozoic, but with some notable exceptions (Hanna, 1927), thick deposits of marine diatomite are middle Tertiary or younger. Nonmarine diatoms occur in rocks as old as late Eocene (Lohman and Andrews, 1968), but most nonmarine diatomite deposits are late Tertiary or Quaternary. The lack of more ancient diatomaceous rocks may be due partly to conversion of the opaline silica of diatom frustules to other forms of silica (Ernst and Calvert, 1969, p. 131). Marine Tertiary porcelaneous rocks that occur in great thicknesses in California almost certainly represent altered diatomaceous rocks (Bramlette, 1946, p. 50; Lohman, 1960, p. 184–185).

Economic diatomite deposits are of three main types: (1) marine rocks that accumulated near continental margins, (2) nonmarine rocks that formed in lakes or marshes, and (3) sediments in modern lakes, marshes, and bogs. Diatomite deposits near Lompoc, Calif. (Industrial Minerals, 1969, p. 14–16, 17, 37; Mulryan, 1936), exemplify the first type; this material formed in a shallow-marine environment in late Tertiary time. Similar marine diatomite deposits occur elsewhere in coastal California, and less pure marine deposits occur extensively in Maryland and Virginia. Diatomite deposits that formed in lakes or marshes in Nevada, Oregon, Washington, and eastern California represent the second type, and diatomaceous sediments in modern lakes, marshes, and bogs in Florida, New Hampshire, and New York (Conger, 1939) belong to the third type. Modern marine sediments are a potential fourth source of diatoms.

PROSPECTING TECHNIQUES

Prospecting for diatomite involves first outlining of areas that contain stratigraphic sequences likely to include diatomaceous strata—for example, the Tertiary and Quaternary lake basins of the Western United States, or the Miocene marine basins of coastal California—followed by examination of outcrop sections in these areas. After diatomite is found, the initial reconnaissance is followed by

trenching and drilling to determine the size of the deposit. Local high-precision surface gravity surveys may be a promising tool for delineating concealed deposits under some circumstances. Because the diatomite in a deposit may vary considerably, especially from bed to bed, a deposit must be sampled carefully throughout its thickness to determine the quality and potential use of the material. Microscopic examination of the rock may be necessary to distinguish diatomite from volcanic ash or from some porcelaneous rocks.

RESOURCES

Diatomite resources are difficult to describe because diatomaceous rocks underlie large areas and include strata of various qualities; even the resources of California, the principal producing area in the United States, have never been computed and classified according to grade. However, diatomite resources of the United States obviously are more than sufficient for many years to come, even allowing for a steady increase in diatomite production. The abundance of the material is evident, for example, if the deposit controlled by one diatomite-producing company at Lompoc, Calif., is considered. This deposit has been described as covering an area of 3–4 square miles and being workable to a depth of 700 feet (Industrial Minerals, 1969, p. 14), which suggests that it could supply world needs for diatomite at the current rate of consumption for several hundred years. On the other hand, factors such as proximity to markets and suitability of the material for specific uses enter into the evaluation of diatomite resources; the location and quality of diatomite deposits seem to be greater factors in the economics of diatomite production than is the amount of material available.

PROBLEMS FOR RESEARCH

The areal and geologic occurrences of diatomite generally are well known, but conditions that affect the thickness and quality of deposits are imperfectly understood. Postdepositional circumstances that affect the quality of diatomite also are uncertain. Clearly, geologic work on diatomite should involve not only the location and classification of deposits, but also should relate the physical features of diatomite to the geologic history of the rock to aid in the discovery of deposits for particular purposes.

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EVAPORITES AND BRINES

By George I. Smith, Charles L. Jones, William C. Culbertson, George E. Ericksen, and John R. Dyni

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ABSTRACT OF CONCLUSIONS

Commodities derived from evaporite and brine deposits include potassium and magnesium compounds, salt, gypsum and anhydrite, calcium chloride, sodium carbonate and sulfate, nitrates, boron, strontium, bromine, and iodine. World and national resources of most evaporite minerals are very large. Some of these resources are adequate for a few centuries at present rates of consumption; others are adequate for thousands of years; still others are virtually unlimited. Very probably within the next several hundred or few thousand years, no evaporite resources will be exhausted or will increase greatly in cost.

Evaporite resources of the United States are large. Unlimited supplies of nitrates, bromine, and magnesium are available from air and sea water. Resources of salt and sodium carbonate appear adequate for thousands of years at present consumption rates. Known supplies of gypsum and anhydrite, sodium sulfate, borates, strontium, iodine, and calcium chloride should be adequate for hundreds of years. Known domestic resources of potassium compounds may be exhausted in 100 years at present consumption rates, but Canadian resources are sufficient to fulfill requirements of North America for thousands of years.

At present world consumption rates, known world resources of potassium salts in marine evaporites are adequate for 5,000 years, and resources of salt, gypsum, magnesium, and calcium chloride are virtually unlimited. Nonmarine evaporites provide known resources of sodium carbonate adequate for thousands of years, sodium sulfate and strontium for hundreds to thousands of years, and borates, nitrates, and iodine for hundreds of years. Brines from wells, lakes, and the ocean provide resources of iodine, bromine, and calcium chloride adequate for hundreds of years. Sea water and air are unlimited and currently are practical sources of magnesium and nitrogen.

INTRODUCTION

Evaporites and brines are the main source of several industrial and agricultural minerals important to the U.S. economy. Their aggregate annual value is about two-thirds of a billion dollars. Some of the minerals are important because of properties attributable to one element in the compound, others because of the properties of the compound itself. The

valuable components of nearly all of these materials were at one time dissolved in large bodies of water. Their present geologic settings reflect the one or more processes by which those dissolved components were concentrated or crystallized into deposits that can, or might be, commercially exploited.

Some of the commodities described in this chapter come from more than one type of evaporite or brine deposit. The largest quantities, however, generally come from one of three types of deposits that have fundamentally similar geologic histories. Potassium compounds, salt, gypsum, and anhydrite mostly come from sediments formed by the evaporation of sea water during the geologic past. Sodium carbonate, sulfate, borate, nitrate, and some iodine and strontium compounds come from sediments and near-surface brines formed by the evaporation of inland bodies of water. Bromine, iodine, calcium chloride, magnesium, and magnesium compounds are mostly extracted from brines derived from sea water, wells, and inland salt lakes. Lithium is also extracted from brines, but is discussed in a separate chapter.

The existing quantities of evaporites and brines provide theoretical resources that are much larger than the amounts that are likely to ever be used. It is difficult, however, to predict this limit. This is true of all commodities, but some unusual factors are involved in assessing commodities extracted from evaporites and brines. One factor is that some commodities can be derived from both evaporites and brines. Future resources of these commodities are thus represented by extremely diverse forms of "ore" which may vary in grade by one or two orders of magnitude. Obviously, they require quite different technologies for processing and therefore very different bases for projecting future use. Brines, in essence, are very low grade ore bodies that are exploitable only because they are very large and can be inexpensively processed. Many brines contain less than 5 percent of the desired substance, and some contain only a few tenths or hundredths of a percent. Solid salts, in contrast, are generally mined from very high grade ore bodies; operating potash mines normally extract ore containing more than 20 percent potassium mineral, and salt, sodium carbonate, and borate mines normally extract ore that is 75–95 percent mineral.

Another reason that resources of commodities obtained from evaporite and brine deposits are difficult to assess is that the price is determined largely by the cost of transporting the commodities to markets. Deposits nearest rail and highway systems now have an advantage over those that are more remote; deposits near seaports have advantages over all others in shipping to some domestic and most international markets. Proximity to markets and efficiency of transportation will probably remain important factors in the economic potential of most deposits, but consideration of these factors is beyond the scope of this study so cannot be included in its conclusions.

Still other uncertainties must be considered in the evaluation of the resources of certain commodities. Some are compounds, not elements, and new technological developments may provide ways in which some of them can be synthesized from abundant and low-cost sources of their ingredients. Still others are present in significant amounts in sea water, and new processes may someday allow them to be extracted from it; sea water would then be an unlimited source of those commodities.

In the following discussion, the geologic settings of evaporite and brine deposits are first outlined. Commodities derived from evaporites and brines are then described individually so that their uses, production, economics, geologic settings, and known resources can be outlined. Speculation follows as to the outlook for existing but undiscovered resources of geologically related commodities; future resources are discussed in genetically related groups because evaluation of them is based more on their general character and on the prevalence of broadly favorable areas than on specific targets. Salient problems and examples of the research necessary to help solve them are suggested in the final section.

GEOLOGIC SETTING OF EVAPORITE AND BRINE DEPOSITS

The deposits that serve as sources of commodities derived from evaporites and brines are grouped in this chapter both by the geologic setting in which they originated and by their present form. Crystalline deposits are separated into two groups according to their marine or nonmarine origin; surface and subsurface waters containing unusual quantities of valuable inorganic components are combined into a group called brines, regardless of their probable geologic origin. Although deposits within each group differ in many respects, they have features in common. The following summaries emphasize the common features but also note some of the differences.

MARINE EVAPORITES

The group of sedimentary rocks known as marine evaporites consists of halite, gypsum, anhydrite, and commonly some interbeds of limestone and dolomite. Some limestone and either gypsum or anhydrite are present in all major and many minor evaporite basins of the United States (fig. 24, table 42); halite and

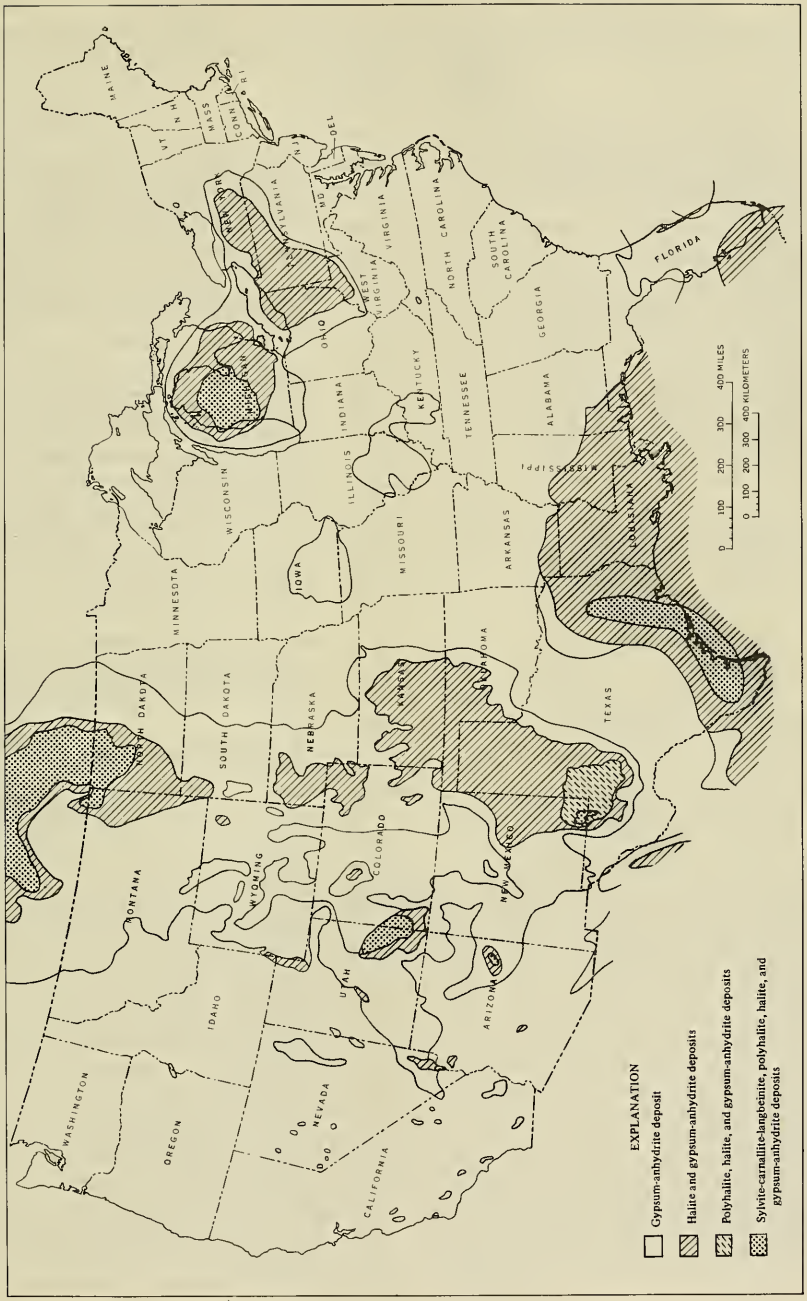

FIGURE 24.—Marine evaporite deposits of the United States.

TABLE 42.—*Marine evaporite deposits of the United States*

[Evaporite minerals are gypsum, G; anhydrite, A; halite, H; polyhalite, P; and the bittern salts of potassium and magnesium (chiefly sylvite, carnallite, and langbeinite), S. Thicknesses are approximate and include nonevaporite rocks]

Age and unit or formation	Evaporite minerals present					Thickness (feet)	Area	Evaporite mineral recovered
	G	A	H	P	S			
Tertiary:								
Muddy Creek Formation	×	×	×	--	--	1,200	Western Arizona shelf (western Arizona, southern Nevada).	Gypsum.
Evaporite-bearing rocks, undifferentiated	×	×	×	--	--	2,000+	Central Arizona	Halite.
Gypsum-bearing rocks, undifferentiated	×	×	×	--	--	400	Various places in Coast Range and Mohave Desert (southern and central California).	Gypsum.
Cedar Keys Limestone	--	×	--	--	--	1,000	South Florida shelf (Florida)	----------
Cretaceous:								
Gypsum-bearing rocks, undifferentiated	×	--	--	--	--	100(?)	Western Arizona shelf (southern Nevada)	----------
Beds of Trinity, Fredericksburg, and Washita age.	×	×	×	--	--	4,200	Florida shelf (Florida)	----------
Ferry Lake Anhydrite	×	×	--	--	--	200	Gulf Region (eastern Texas to Alabama)	----------
Hell to Finish Formation of Zeller (1958, 1965)	×	×	--	--	--	100(?)	Northwestern shelf of Chihuahua trough (southwestern New Mexico).	----------
Cretaceous(?) or Jurassic(?):								
Fort Pierce Formation	--	×	--	--	--	1,800	South Florida shelf (Florida)	----------
Jurassic:								
Todilto Limestone	×	--	--	--	--	100	Lacustrine(?) basin (northwestern New Mexico).	Gypsum.
Malone Formation	×	×	--	--	--	25	Chihuahua trough (western Texas)	----------
Minas Viejas Group of Mexico	×	×	×	--	--	1,500	Rio Grande embayment (southern Texas)	----------
Buckner Formation	×	×	×	--	--	150	Gulf region (eastern Texas to Alabama)	----------
Werner Formation and Louann Salt (Jurassic age uncertain).	×	×	×	--	×	4,000+	Gulf region (Texas to Alabama and Florida Panhandle).	Gypsum, halite.
Curtis, Summerville, and Wanakah Formations	×	×	--	--	--	150	Utah shelf (central and southwestern Utah and western Colorado).	----------
Preuss Sandstone	×	×	×	--	--	700	Western Wyoming-Idaho trough (northern Utah, southeastern Idaho, and southwestern Wyoming).	----------
Carmel Formation	×	×	--	--	--	150	Utah shelf (central and southwestern Utah)	----------
Arapien Shale	×	×	×	--	--	200+	Utah shelf (central Utah)	Gypsum, halite.
Twin Creek Limestone	×	×	--	--	--	100	Western Wyoming trough (Wyoming and Idaho).	----------
Piper Formation	×	×	--	--	--	125	Northern Rocky Mountain shelf (Montana)	Gypsum.
Gypsum Spring Formation	×	×	×	--	--	125	Williston basin and southwestern shelf (Montana, North and South Dakota, and Wyoming).	Gypsum.
Triassic:								
Gypsum-bearing rocks, undifferentiated	×	×	--	--	--	?	Cordilleran eugeosyncline (northwestern Nevada, central-eastern Oregon, and western Idaho).	Gypsum.
Moenkopi Formation	×	×	--	--	--	600	Western Arizona shelf (southwestern Utah, northwestern Arizona, and southern Nevada).	----------
Triassic and Permian:								
Goose Egg Formation	×	×	×	--	--	300	Northwestern shelf of Denver basin (Wyoming and Colorado).	Gypsum.
Spearfish Formation	×	×	×	--	--	400	Williston basin (Montana and North and South Dakota).	----------
Triassic(?) and Permian:								
Lykins Formation	×	×	--	--	--	150	West side of the Denver basin (Colorado)	Gypsum.
Permian:								
Rustler, Salado, and Castile Formations	×	×	×	×	×	4,100	Southern Permian basin (New Mexico and Texas).	Sylvite, halite.
Artesia Group	×	×	×	--	--	1,100	Northern and western shelf of Delaware basin (New Mexico).	----------
Artesia Group	×	×	×	--	--	1,100	Eastern shelf of Permian basin (Texas)	----------
San Andres Limestone	×	×	×	--	--	1,000	Central Permian basin (Texas and New Mexico).	----------
Blaine Formation	×	×	--	--	--	300	Northern and eastern Permian and Anadarko basins (Kansas, Oklahoma, and Texas).	Gypsum.
Briggs Formation	×	×	--	--	--	600	Diablo platform (Texas)	----------
Pequop and Loray Formations of Steele (1960)	×	×	--	--	--	500	Cordilleran miogeosyncline (eastern Nevada and western Utah).	----------
Undifferentiated saline-bearing rocks of Permian age.	×	×	--	--	--	800	Western Arizona shelf (western Arizona and southern California).	Gypsum.
Kaibab Limestone	×	×	--	--	--	300	Western Arizona shelf (southern Nevada, southwestern Utah, and western Arizona).	----------
Toroweap Formation	×	×	--	--	--	400	Western Arizona shelf (southern Nevada, southwestern Utah, and western Arizona).	----------
Opeche Shale	×	×	×	--	--	250	Williston basin (Montana and North and South Dakota).	----------
Yeso Formation	×	×	×	--	--	1,000	Northwestern shelf of Delaware basin (New Mexico).	----------
Clear Fork Group and Flowerpot Shale	×	×	--	--	--	1,500	Northern and central Permian basin (Kansas, Oklahoma, Texas, and Colorado).	----------
Epitaph Dolomite and equivalents	×	×	--	--	--	300	Sonoran trough (southeast Arizona and southwestern New Mexico).	----------
Wichita and Wellington Formations; Hennessey and Ninnescah Shales; Stone Corral Formation	×	×	×	--	--	800	Northern and central Permian basin and Anadarko basin (Kansas, Nebraska, Colorado, and Oklahoma).	Halite, gypsum.
Abo Formation	×	×	--	--	--	200	Northwestern shelf of Delaware basin (New Mexico).	----------
Supai Formation	×	×	×	--	×	1,000	Shelf (east-central Arizona)	----------
Pakoon Limestone of McNair (1951)	×	×	--	--	--	200	Western Arizona shelf (southern Nevada)	----------
Easly Creek Shale	×	×	--	--	--	20	Northern Permian basin (Kansas)	Gypsum.
Permian(?):								
Fort Dodge Gypsum of McGee (1884)	×	--	--	--	--	50	Northeastern shelf of Forest City basin (Iowa).	Gypsum.

TABLE 42.—*Marine evaporite deposits of the United States*—Continued

Age and unit or formation	Evaporite minerals present					Thickness (feet)	Area	Evaporite mineral recovered
	G	A	H	P	S			
Permian and Pennsylvanian:								
Minnelusa Formation	×	×	×	--	--	450	Denver and Williston basins (Colorado, Nebraska, North and South Dakota, and Montana).	----------
Wells Formation	--	×	--	--	--	100	Southeastern Idaho and northern Utah	----------
Panther Seep Formation	×	×	--	--	--	100	Oro Grande basin (southern New Mexico)	----------
Pennsylvanian:								
Hermosa Formation	×	×	×	--	×	5,000	Paradox basin (Colorado and Utah)	Sylvite, halite.
Eagle Valley Evaporite	×	×	×	--	×	1,000	Eagle basin (western Colorado)	----------
Mississippian or younger:								
Gypsum-bearing rocks, undifferentiated	×	×	--	--	--	50(?)	Cordilleran eugeosyncline (Chichagof Island, Alaska).	----------
Mississippian:								
Big Snowy Group (of formation rank in SW Montana and Idaho).	×	×	--	--	--	50	Northern Rocky Mountain shelf (Montana, Idaho, and Wyoming).	----------
Otter Formation	×	×	--	--	--	50	Williston basin and Northern Rocky Mountain shelf (Montana and North and South Dakota).	----------
Kibbey Formation	×	×	--	--	--	200	Williston basin and Northern Rocky Mountain shelf (Montana and North and South Dakota).	----------
Charles Formation	--	×	×	--	--	800	Williston basin and Northern Rocky Mountain shelf (Montana and North and South Dakota).	----------
Warsaw and St. Louis Limestones	×	×	--	--	--	125	Northeastern shelf of Forest City basin (Iowa).	Gypsum.
St. Louis Limestone	×	×	--	--	--	200	Illinois basin (Indiana, Illinois, and Kentucky).	Do.
Maccrady Shale	×	×	×	--	--	250(?)	Appalachian basin (Virginia)	Gypsum, halite.
Michigan Formation	×	×	--	--	--	450	Michigan basin (Michigan)	Gypsum.
Devonian:								
Three Forks Formation and Potlatch Anhydrite	--	×	--	--	--	480	Northern Rocky Mountain shelf (Montana)	----------
Souris River Formation	--	×	--	--	--	200	Williston basin (Montana and North and South Dakota).	----------
Prairie Formation	×	×	×	--	×	600	Williston basin (Montana and North and South Dakota).	(Halite and sylvite recovered in Canadian aection of basin).
Cedar Valley and Wapsipinicon Limestones	×	×	--	--	--	300	Northeastern shelf of Forest City basin (Iowa).	Gypsum.
Detroit River Group (of formation rank in Indiana according to Shaver and others, 1970).	×	×	×	--	--	1,100	Michigan basin (Michigan, Ohio, and Indiana).	Halite.
Silurian:								
Salina Formation	×	×	×	--	×	4,000	Appalachian and Michigan basins (New York, Pennsylvania, West Virginia, Ohio, and Michigan).	Gypsum, halite.
Silurian and Ordovician:								
Interlake Formation	--	×	--	--	--	50	Williston basin (Montana and North and South Dakota).	----------
Ordovician:								
Red River, Stony Mountain, and Stonewall of Kindle (1914) Formations.	--	×	--	--	--	200	Williston basin (Montana and North and South Dakota).	----------
Joachim Dolomite equivalent	--	×	--	--	--	85	Illinois basin (Illinois)	----------
Precambrian:								
Grenville Series	×	×	--	--	--	200	Northwestern Adirondack Mountains (New York).	----------

potassium minerals are present in some. Evaporites typically form stratified rock units that extend tens and even hundreds of miles and attain thicknesses of several thousand feet (Pierce and Rich, 1962; Withington, 1962). Many deposits occupy areas that were part of the continental shelf and that extend into areas that were part of an adjacent synclinal trough. Locally, along the continental margin and elsewhere, great masses of halite and associated evaporites have intruded overlying sedimentary strata to form salt domes and other diapiric structures. Both bedded and domal deposits of marine evaporites are known to contain potassium ores, and they are also important sources of gypsum, anhydrite, salt, sulfur, and other commodities (Stewart, 1963; Braitsch, 1971).

All marine evaporites are thought to have been formed by evaporation of sea water in barred basins or on broad shelf areas where circulation was restricted. The dominant rocks formed in this manner were limestone, dolomite, gypsum or anhydrite, halite, and the rocks containing potassium minerals. Within most evaporite basins, these rocks are arranged in broad belts or facies that reflect the changing depositional environment between open sea and land; limestone or dolomite facies lie in the areas that contained the least saline water, and they grade into gypsum or anhydrite facies, then to halite facies, in areas that contained successively more saline waters. Red beds commonly represent the nearshore accumulation of clastics. Economic concentrations of potassium minerals represent the final stage of evaporite deposition and wherever present lie within the halite facies (Mattox and others, 1968; Hite, 1970).

Examples representing virtually all possible distributions of evaporite facies are found in evaporite basins of the United States. Potassium minerals typically occupy only a small part of a basin and are relatively rare; only 7 of the 69 marine evaporite deposits listed in table 42 are known to contain potassium minerals. Halite facies are found in 28 of the 69 deposits listed in that table. Gypsum or anhydrite facies are found in all.

NONMARINE EVAPORITES

Nonmarine evaporite deposits include near-surface saline minerals (and associated brines) in Quaternary dry lakes, and bedded crystalline deposits in continental Tertiary formations. Pre-Tertiary deposits are known, but are rare and much less important. All are geologically similar in that they formed by evaporation of lakes in closed basins. The geologic requirements for such deposits are: (1) development of a closed basin that prevents the components dissolved in the waters from escaping to the sea, and (2) an original mixture of dissolved components that evolves by means of successive crystallizations into a concentrated brine that precipitates valuable salts.

Basins having no external drainage are mostly products of faulting or warping. To persist, they require a tectonic setting that will either lower the floor of the basin faster than sedimentation can raise it or elevate barriers across possible outlets faster than erosion can destroy them. Most, but not all, closed basins today are in arid or semiarid areas where sedimentation rates are low. Comparable basins in the geologic past probably had a similar climatic setting.

For valuable evaporite deposits to form in a closed basin, however, enough water must have flowed into the basin to introduce large quantities of salts. This requirement greatly limits the number of highly favorable environments because arid basins generally receive large volumes of water only where they adjoin high mountain ranges or are the terminus of integrated drainages from adjacent less arid regions. Even when these conditions are satisfied, most waters will not evolve through natural evaporation into a lake containing a valuable mix of components. The most favorable source waters for a sodium carbonate deposit, for example, come from springs or from rivers draining volcanic terrane, although metamorphic and some other igneous terranes are suitable. Apparently a sodium carbonate lake cannot be formed by evaporation of calcium bicarbonate waters from limestone terrane, of sulfate waters from sulfide deposits, or of chloride waters from marine evaporites (Eugster, 1971, p. B46).

The minerals deposited depend upon the composition and temperature of the brine at the time of crystallization. Normally, saline minerals are formed in a sequence that is determined by their solubility in the particular chemical and physical environment provided by the lake. Studies of sodium carbonate deposits, for example, find that these minerals generally crystallize after the calcium-bearing minerals and before the sodium sulfate and chloride minerals, although the sequence varies. The species of carbonate mineral formed depends on the partial pressure of dissolved CO_2 in the brine. If the brine is in equilibrium with the partial pressure of CO_2 in the atmosphere, trona ($Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$) is formed; if the partial pressure is higher because of organic activity, nahcolite ($NaHCO_3$) is formed; if lower, natron ($Na_2CO_3 \cdot NaH_2O$) is formed (Bradley and Eugster, 1969). Because of diagenesis after burial, the carbonate mineral constituting the final deposit tends to reflect the CO_2 pressures in the accumulating bed of minerals rather than in the open lake waters.

BRINES

Many of the brines that are exploited commercially contain abnormally large amounts of bromine, iodine, calcium chloride, and magnesium. The geologic processes that result in such brines have long been debated and are not well understood today. Probably several processes were operative inasmuch as the brines come from diverse geologic settings; some of the brines are pore waters in oil fields, some are deep-well brines from marine salines or rocks peripheral to them, some are from thermal springs or wells, and some are surface or subsurface brines that were associated with Quaternary salt lakes or seas. The geologically old and deep-well brines were probably produced chiefly during diagenesis by the interaction of pore fluids with clays and possibly with other components of clastic rocks that act as ionic filters; some of the fluids may have originally been sea water of normal salinity although most were probably bitterns from marine evaporites (White, 1957, 1965; White and others, 1963; Rittenhouse, 1967; Collins and others, 1967). Quaternary brines that contain abnormally large amounts of bromine and other substances are products of natural evaporation of dilute river and spring waters that mostly originally had unusually high ratios of these components (Bentor, 1961; Livingstone, 1963; Jones, 1966; Hardie and Eugster, 1970).

KNOWN RESOURCES OF EVAPORITES AND BRINES

POTASSIUM COMPOUNDS

Potassium (commonly referred to as its oxide, "potash," K_2O) is a plant nutrient that is essential to maintain and expand food production for both man and animal. About 95 percent of the potassium compounds produced in the world are used as fertilizers; the remaining 5 percent are used in manufacturing drugs, dyes, and chemical reagents (U.S. Bur. Mines, 1970). Polyhalite ($2CaSO_4 \cdot K_2SO_4 \cdot MgSO_4 \cdot 2H_2O$) deposits in New Mexico and Texas are not now used, but may someday be, as a combination soil conditioner and fertilizer; coarsely ground polyhalite in contact with water forms solutions containing potassium, magnesium, and sulfate, and leaves gypsum as a soil-conditioning residue.

World production of potassium compounds in 1970–71 was equivalent to 17.8 million tons of K_2O, and production capacity is considerably larger. Eastern Europe supplied 37 percent of this quantity; North America, 31 percent; Western Europe, 27 percent; and South America, Africa, and Asia, the balance. Countries providing major sources are the U.S.S.R., East Germany, West Germany, France, Canada, and the United States. Israel, Spain, Italy, China, Chile, and Congo (Brazzaville) provided smaller amounts. Potash-producing facilities are under development in Australia and the United Kingdom (Eilertsen, 1971; Lewis, 1970b; British Sulphur Corp., 1971).

In the United States in 1970, potassium compounds were produced by 13 companies which operated plants in five States. About 87 percent of production in the United States comes from crystalline deposits in southeastern New Mexico and eastern Utah; the remaining 13 percent comes largely from brine operations in northwestern Utah, California, and Michigan. Production declined from a maximum of 3.3 million tons of K_2O equivalent valued at $122 million in 1966 to 2.7 million tons valued at about $71 million in 1970 (Lewis, 1970b). This decline is expected to continue as the domestic industry faces serious problems of dwindling reserves of high-grade ores and loss of markets to Canadian sources of supply.

Sources of potassium compounds in the United States and elsewhere in the world are of two main types: (1) crystalline deposits of saline rocks of marine origin containing sylvite, langbeinite, and related potassium minerals, and (2) concentrated brines from wells or in relict lakes and lacustrine sediments of continental origin in arid regions. The crystalline deposits are by far the richest in potassium and the simplest to exploit; the concentrated brines are lower grade but generally allow production of other substances such as sodium carbonate, sodium sulfate, borates, magnesium, lithium, or bromine as coproducts of the potassium compounds.

Most potassium ores in marine evaporite deposits have the potassium concentrated in sylvite (KCl) or a potassium-magnesium mineral, and all occur within the sodium-rich (halite) facies of evaporite deposits. Although not now considered ore, large and nearly pure deposits of the potassium mineral polyhalite ($K_2MgCa_2(SO_4)_4 \cdot 2H_2O$) occur in or near the calcium-rich facies of evaporite deposits. In North America, polyhalite deposits occur only in southeastern New Mexico and western Texas near the boundary of the halite and anhydrite facies.

The greatest concentrations of sylvite in most evaporite basins are in tabular bodies that may be primary or replacement in origin. Such deposits are mostly tens of feet thick and several square miles in area, and generally contain at least twice as much halite as sylvite. Smaller concentrations of sylvite (or carnallite) occur in markedly discordant replacement lenses and veins that contain little or no halite. Both types of concentrations ordinarily have sharp, clear-cut boundaries (Jones and Madsen, 1968).

Brines are also a source of potassium compounds in the United States. Most productive brines are from inland lakes but some are from deep wells. Most allow production of other commodities along with the potassium salts so that the costs of processing are shared, a practice that contributes to the commercial feasibility of such low-grade sources of the element. In other respects, however, brines that yield potassium have little else in common, either geologically or chemically. Production from California is from alkaline near-surface brines in an upper Quaternary saline deposit; Utah production is from nearly neutral surface waters of a saline lake; Michigan production is from acidic deep-well brines; production from Israel is from brines in the Dead Sea.

Exploration for potassium deposits is difficult because the deposits are soluble and consequently do not crop out at the surface. Before extensive drilling for petroleum, potassium deposits were mostly encountered accidentally in mines being worked for salt. Analysis of near-surface brines from relict lakes has been used with some success to locate exploitable deposits in arid regions, but it has not been used with success elsewhere. Analysis of cuttings, cores, and gamma-ray and other logs from exploratory boreholes drilled primarily for petroleum has been responsible for most potash discoveries in recent

years, and the recognized association of petroleum and evaporites means that a high percentage of basins favorable for evaporites in North America have been explored by oil companies (Buzzalini and others, 1969). The potash deposits in southeastern New Mexico, eastern Utah, and southern Saskatchewan—mines which now supply roughly one-third of all the world output of potassium compounds—were discovered in this way.

Many geologic guides to the locations of concealed potassium salts and other evaporites are available. Preliminary evaluation techniques include reconstructing from geologic maps and other sources the climatic, topographic, hydrologic, and geochemical environments that existed at the time the sedimentary rocks in the particular basin were deposited. Arid climatic belts that favor deposition of evaporites tend to occupy the same part of the globe, and paleomagnetic and other techniques allow the geographic positions of depositional basins relative to these belts to be reconstructed. Sedimentary rock units that are most favorable for evaporites are those that were deposited at latitudes favorable for arid climates. Many other characteristics and constituents of sedimentary rocks indicate the climate that prevailed during sedimentation; for instance, certain organisms and chemical reactions are temperature sensitive, and microfossils or other organic materials, stable isotope percentages, and mineralogy may therefore give data as to water temperature. Still other prospecting techniques depend on interpretational refinements of many kinds of field data. Within favorable climatic belts, environments capable of forming marine evaporite deposits were the nearly enclosed basins and shallow shelf areas that lay between the open sea and the landmasses. Systematic geologic mapping furnishes data essential to the reconstruction of paleogeographic environment. Processes involved in chemical sedimentation and diagensis are also becoming better understood. Once an evaporite body has been found, numerous exploratory techniques can expedite the location of high-grade potassium deposits. Evaporite mineral facies have a fairly predictable pattern, and variations in the quantities of certain trace elements such as bromine can indicate areas and horizons of maximum promise.

At present production levels, potash reserves available in crystalline deposits and brines within the United States are sufficiently large to last at least 100 years. The very large deposits of Canada, however, are so close to the United States that costs of transporting supplies from these deposits are not excessive; inasmuch as one-half of the world reserves and resources are in Canada, resources adequate for thousands of years will continue to be available from areas close to U.S. consumers. Potential resources of the United States also are large and include submarginal crystalline deposits, sea water, and potassium-bearing silicate rocks (British Sulphur Corp., 1966).

World reserves and potential resources of potassium compounds are enormous. Estimates of quantities in known deposits exceed 100 billion tons of K_2O; this represents more than a 5,000-year world supply at present consumption rates (Colorado School of Mines, 1967). Hypothetical and undiscovered deposits increase the total probable resources to a larger quantity, but as noted later, this increase may not be great.

SALT

Among the marine evaporites, salt (the common term for both the commodity and rock composed entirely of halite, NaCl) is by far the most valuable mineral resource, ranking with coal, limestone, iron, and sulfur, as a basic industrial raw material. It is used as a source of sodium, chlorine, soda ash, hydrochloric acid, caustic soda, and other compounds indispensable in the manufacture of many other products and chemical reagents. Salt itself is important in the production and preservation of foodstuffs as well as for animal feed, water softening, snow and ice removal, and roadbed stabilization (Hibpshman, 1971). Underground cavities created artificially in rock salt deposits are used to store petroleum products and to dispose of industrial wastes; the resource value of some salt deposits may be determined more by the possible storage capacity than by the need for the salt that was removed to provide that capacity (Pierce and Rich, 1962).

In the United States, leader of world production of salt, more than 45 million tons of salt with a value of more than $285 million was produced in 1970 by 54 companies, which operated 99 plants in 17 States. China, the U.S.S.R., Germany, and the United Kingdom are the other major producers. Australia has had the greatest recent increase in production (Jacoby, 1972). Past growth of the industry has been steady, and the future outlook is for an annual growth of from 3 to 5 percent.

The principal methods of producing salt in the United States are (1) solution mining, (2) underground mining, and (3) evaporation of natural brines and sea water. About 70 percent of the salt produced in the United States is extracted from natural or synthetic brines or sea water; 30 percent is mined as a solid (Kaufmann, 1960).

Subsurface deposits of rock salt are the principal

source of salt in the United States. About half of the production is from salt domes, and most of the balance from stratified marine evaporites. Boreholes show that stratified halite deposits occur in most major evaporite basins and a few minor basins that are distributed through 24 of the 50 States. The deposits are typically extensive and thick, and tend to be superposed one above the other over wide areas (fig. 24 and table 42). Few domes or beds are pure salt, but their salt content may exceed 98 percent; dolomite, shale, anhydrite, and other evaporites are usually found as impurities. Individual beds in stratified rock salt range in thickness from a fraction of an inch to several hundred feet, and they are both massive and laminated. Salt domes have very complex internal structures.

Salt is also produced in the United States from salt lakes in the arid Western States and by solar evaporation of sea water. Unpurified salt scraped from dry lakes normally contains small amounts of other components that limit its use or require purification. Nearly pure salt is produced by solar evaporation of lake brines and sea water, but the process requires an arid climate and large flat areas for evaporation ponds (Ver Planck, 1958).

Domestic resources of salt are virtually unlimited (Lefond, 1969). Huge bedrock resources are known in the Northeastern, Southeastern, and Central Western States (fig. 24); salt lakes and solar evaporated sea salt are close to populated areas of the west coast states.

Salt resources of the rest of the world are also virtually unlimited. About 15 percent of the earth's continental areas are underlain by beds of marine salt (Kozary and others, 1968) that can be extracted by excavation or solution mining as the need arises. Even greater quantities could be extracted from sea water. This conclusion does not mean that salt will be extracted from sursurface layers or adjacent seas by all countries that have these resources, because the economics of producing and transporting the product will remain dominant. What it does mean is that requirements can be met if necessary for even remotely foreseeable future demands.

GYPSUM AND ANHYDRITE

Gypsum ($CaSO_4 \cdot 2H_2O$) and anhydrite ($CaSO_4$) are common evaporite minerals widely used in the construction industry and agriculture. Gypsum, by far the more important of the two, is used to retard setting time in portland cement and as an agricultural soil conditioner and fertilizer. In addition, gypsum is calcined for use as plaster for construction and industrial purposes, and for manufacturing wallboard and other prefabrication products widely used in the building industries. Anhydrite is interchangeable to a limited extent with gypsum for use as a soil conditioner. In Europe and elsewhere, anhydrite has had moderate use in manufacturing sulfuric acid and ammonium sulfate.

For more than a decade, the United States has produced annually about 25 percent of the world gypsum supply, and at the same time it has been dependent on foreign sources for about one-third of its gypsum supply. Domestic production for the past 10 years has ranged between 9.4 and 10.7 million tons per year, with its annual value ranging mostly between $35 and $40 million. Imports, chiefly from Canada, Jamaica, and Mexico, have averaged almost 5.6 million tons per year (Ashizawa, 1971). Approximately 50 percent of the domestic gypsum supply comes from mines and quarries in Michigan, Iowa, Texas, and California; the remainder is from mining operations in 17 States. Both the domestic production and the imports of gypsum are very sensitive to the demands of the construction industry, and they respond rapidly to any change in the activity of this industry (Schroeder, 1970).

Both gypsum and anhydrite occur widely and abundantly in virtually all marine evaporite basins (Withington, 1962). Gypsum normally predominates over anhydrite at or near the surface and grades into anhydrite at depths ranging from a few feet to a few hundred feet. Geological evidence indicates that some near-surface gypsum was formed by hydration of primary or secondary anhydrite where meteoric ground and surface water came in contact with anhydrite. The depth of complete hydration is important in exploitation because the presence of more than a few percent anhydrite renders gypsum unfit for many purposes.

Some gypsum is mined from deposits formed in continental basins by the evaporation of nonmarine waters. Most of these deposits probably originated as gypsum, and their lack of deep burial has kept anhydrite from forming. Most nonmarine deposits are smaller than marine deposits but tend to be nearer the surface.

Domestic reserves and resources of gypsum are plentiful but are unevenly distributed. They are concentrated in the eastern Great Lakes region, the central midcontinent region, the Rocky Mountain belt from Canada to Mexico, and the southern California and Nevada region. Like salt, beds of gypsum also underlie an appreciable part of the earth's continents; but unlike salt, they cannot be mined by solution and must therefore lie near the surface to be extracted at low cost. Nevertheless, available quanti-

ties are very large and adequate for centuries to come. Synthetic gypsum is produced as a byproduct of the manufacture of several other compounds, but the economics of production probably will prevent these sources from being exploited solely for the value of the gypsum.

SODIUM CARBONATE

Sodium carbonate (Na_2CO_3, which is known industrially as "soda ash") is an important industrial chemical because of its own chemical properties, and because of its use in the manufacture of other compounds such as sodium bicarbonate, sodium hydroxide, and sodium nitrate. In 1970 the United States consumed 6.8 million tons of sodium carbonate and exported an additional 0.3 million tons. Present domestic consumption is as follows: 50 percent for manufacture of glass, 40 percent for making other chemicals, 8 percent in paper and pulp manufacture, and 2 percent in miscellaneous uses such as soap, detergents, and water softeners (MacMillan, 1970d; Lansche, 1971b). A potentially large use of one of its derivatives, sodium bicarbonate ($NaHCO_3$), is as a cleanser of sulfur dioxide from stack gases of powerplants.

Most of the sodium carbonate and bicarbonate now produced in the United States is manufactured from sodium chloride, ammonia, and carbon dioxide by the Solvay process, but this production is gradually declining because of the high cost of new plants and pollution problems. This chapter discusses natural deposits whose 1971 production was valued at $56 million and constituted 38 percent of the U.S. total. Before 1950, sodium carbonate from natural sources in California supplied only about 6 percent of U.S. needs. In that year, however, production commenced from an immense deposit of bedded trona ($Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$) in southwestern Wyoming. By 1970, this deposit furnished about one-third of the Nation's sodium carbonate. It will probably become the major domestic source within a few years; planned increases in the mining and refining capacity of three plants producing from the Wyoming deposit would raise annual production to about 5 million tons of sodium carbonate (70 percent of present consumption) and a possible fourth plant would raise production even further.

Core drilling is virtually required in prospecting for natural sodium carbonate and other saline deposits. All valuable saline minerals are soluble and so are rarely exposed in outcrop, but some geologic indications help narrow the target before drilling (Smith, 1966c; Culbertson, 1971). For example, sodium carbonate minerals dissolved from outcrops may be indicated by identifiable cavities or pseudomorphs, a high sodium carbonate content in ground or surface water may indicate concealed deposits undergoing such solution, and certain lithologic textures and less soluble evaporite minerals in outcropping rocks may indicate nearby buried salines. Gamma-ray, neutron, sonic, and density geophysical logs from oil and gas test holes generally indicate the presence of any trona layers that were penetrated, although it is difficult to distinguish them from some other evaporites.

The domestic resources of sodium carbonate are immense. Not only are there nearly inexhaustible supplies of salt and limestone from which sodium carbonate could be manufactured by the Solvay process, but the trona deposits in the Green River Formation of Eocene age in southwestern Wyoming that are now being mined would supply the Nation's needs for more than 3,000 years at the present rate of consumption. These deposits underlie an area of about 1,300 square miles at depths of 400–3,500 feet (Bradley and Eugster, 1969; Culbertson, 1971). Resources of trona in beds more than 3 feet thick total about 85 billion tons; some beds, however, locally contain halite as an impurity. Between 30 and 40 billion tons of trona are contained in halite-free beds more than 6 feet thick. Marlstone and oil-shale beds between the trona beds contain submarginal resources in the form of disseminated sodium carbonate minerals such as shortite ($Na_2CO_3 \cdot 2CaCO_3$) and northupite ($Na_2CO_3 \cdot NaCl \cdot MgCO_3$).

In northwestern Colorado, the Green River Formation contains additional resources of sodium carbonate in the form of nahcolite ($NaHCO_3$). These resources add substantially to the nation's supply. The mineral occurs as lenses, nodules, and beds in a thick sequence of rich oil shale that also contains large amounts of dawsonite and some halite. Nahcolite-bearing oil shale, 100 or more feet thick, underlies an area of about 255 square miles in the northern part of the Piceance Creek basin at depths of 1,100–2,000 feet. The average nahcolite content in representative core holes ranges from 13 to 26 weight percent. The area is estimated to contain 32 billion tons of nahcolite, making this the second largest sodium carbonate deposit known in the world (Trudell and others, 1970; Dyni and others, 1970). Nahcolite is a potential source of soda ash, but it may also gain use in its natural form as a chemical agent for removing oxides of sulfur and nitrogen from hot industrial stack gases and as a low-cost means of increasing the yield of alumina from interbedded dawsonite-bearing oil shales with which the nahcolite necessarily would be mined.

Searles and Owens Lakes, Calif., contain amounts of sodium carbonate smaller than those in Colorado. The deposits are of Quaternary age and consist of porous crystalline bodies saturated with brines (Smith, G. I., 1966a). They are estimated by us to contain about 700 million tons of sodium carbonate. Some sodium carbonate occurs in numerous small playa lakes in the Western United States; the resource potential of these deposits probably does not exceed 200 million tons (Garrett and Phillips, 1960).

Production of sodium carbonate from natural sources also comes from the trona deposits of Lake Magadi, Kenya (Eugster, 1970). The lake generates new trona at about the same rate as present annual production (150,000–200,000 tons). Other sodium carbonate lakes in the rift valleys of eastern Africa contain large but unknown amounts of additional material. Deposits of unknown, but probably small, size occur also in South America, eastern Europe, the U.S.S.R., central Africa, China, and India.

SODIUM SULFATE

Sodium sulfate (Na_2SO_4, known also as "salt cake"), is produced in the United States from natural brines and as a byproduct of certain manufacturing processes. About 1.5 million tons is produced annually of which 46 percent, valued at $12.5 million, comes from natural sources in California, Utah, Texas, and Wyoming (Lansche, 1971b; MacMillan, 1970d). The kraft paper industry consumes nearly 75 percent of U.S. production whereas the glass, ceramic glaze, detergent, and other industries consume the balance (Goudge and Tompkins, 1960).

California sodium sulfate production from natural sources comes from subsurface Pleistocene brines in Searles Lake; Utah production is from the brines in Great Salt Lake; Texas production is from subsurface brines; and Wyoming production is from surface crusts on dry lakes. Canadian production, which is about equal to U.S. production from natural sources, comes from salt lakes in Saskatchewan. All deposits are in arid to semiarid environments. The presence of sodium sulfate in a closed basin is a result of several geologic controls, especially the chemical composition of rocks and soils within the drainage area and the composition of mineral springs that discharge into the basin. Extraction processes can be relatively simple because of the marked influence of temperature on the solubility of sodium sulfate at temperatures below 32°C (Rueffel, 1970).

Resources of sodium sulfate are large. Searles Lake, Calif., is estimated by us to contain 400 million tons, a 600-year supply at present rates of U.S. consumption from natural sources. Great Salt Lake contains about 30 million tons, and both solid and brine deposits are known in 10 other States in the United States. Canadian deposits contain about 60 million tons. Production has come also from several countries in Europe and South America, and a single deposit in the U.S.S.R. contains an estimated 2 billion tons (Goudge and Tompkins, 1960).

BORON MINERALS

Boron minerals mined in the United States in 1970 supplied more than 60 percent of world needs. Production totaled about 1 million short tons of ore which contained about 560,000 tons of B_2O_3; value of the ore was approximately $85 million (Kistler, 1972). All domestic production came from California; small deposits in Nevada and Oregon are unmined (Smith, W. C., 1960, 1962). Foreign production came mostly from Turkey with smaller amounts coming from Italy, Argentina, and probably China and the U.S.S.R.

Boron mineral consumption by the United States was about 35 percent of world production. Consumption was largely by the manufacturers of glass, glass fiber, enamel, chemical and agricultural products, soaps and detergents, abrasives, gasoline additives, fire-retardants, metal alloys, and other industries (West, 1971). Annual growth in U.S. consumption over the next quarter century is estimated to be 3.5–4.6 percent, with greater growth possible (MacMillan, 1970a).

Boron minerals being mined today occur chiefly as deposits in nonmarine Cenozoic rocks. Production at Boron, Calif., comes from a thick, slightly deformed lacustrine deposit of middle Tertiary age that contains borax ($Na_2B_4O_7 \cdot 10H_2O$) and kernite ($Na_2B_4O_7 \cdot 4H_2O$) (Barnard and Kistler, 1966). The near lack of other evaporite components in the deposit indicates that it was formed from lake waters unusually rich in sodium borate, but the existence of comparable deposits in Turkey and Argentina show that this setting is not unique. Production near Death Valley, Calif., consists mostly of calcium borates (such as colemanite) from deformed upper Cenozoic mudstone and sandstone deposited in a depression ancestral to Death Valley (McAllister, 1970). Sodium borate production from Searles Lake, Calif., comes from brines pumped from the interstices of mineralogically complex salt layers beneath the dry lake surface; the salts are an upper Quaternary deposit formed by desiccation of a succession of large Pleistocene lakes (Smith, G. I., 1966c). Less is known of the geologic setting of major deposits in other parts

of the world, but available data suggest that most deposits are in areas characterized by above-average amounts of boron in spring waters and sediments and are in Cenozoic nonmarine basins formed by tectonic processes.

Prospecting for boron minerals starts with the identification of basins that were, during the geologic past, favorable for the accumulation of borate-rich waters. Some basins and their sediments are undeformed whereas others are folded, faulted, partly eroded, and concealed to an extent that their original shape can be inferred only by geologic reconstruction. Exploration generally requires drilling. Sodium borate minerals (for example, borax) are soluble and therefore are soon leached from outcrops except in very arid regions. Calcium borate minerals (for example, colemanite) and sodium-calcium borates (for example, ulexite) are less soluble but are not well preserved in outcrop.

Reserves and known resources of borates are large. One published estimate of world indicated reserves is 72 million short tons B_2O_3; one-half of this is in domestic deposits and one-sixth is in Turkish deposits (MacMillan, 1970a, p. 882). Conservative estimates of the sodium borate reserves in California alone show that they are sufficient for 300 years at present domestic consumption rates and 100 years at present world consumption rates (Smith, W. C., 1966). Recently discovered Turkish sodium borate reserves increase this supply fivefold (Industrial Minerals, 1970). Calcium borate reserves in California, Turkey, and South America further add to the supply. At present consumption rates, world reserves and known resources thus are adequate for many hundreds and possibly thousands of years. The geologic settings of boron deposits are relatively well understood, and prospecting during the last decade for new deposits has been correspondingly effective. New deposits are likely to be found if economic incentive exists, and world resources might ultimately be increased 2–10 times.

NITRATES

Nitrogen compounds are essential to modern industry and agriculture. Production of nitrogen compounds by "fixation" of nitrogen from the atmosphere began during World War I and now accounts for all United States, and nearly all world, production of nitrogen compounds. In 1968, world production was 35.4 million tons of contained nitrogen, and U.S. production was 10.1 million tons (Lorenz, 1971). Nitrogen from the atmosphere will supply world needs for the foreseeable future. For nearly 100 years before World War I, however, the chief source of fixed nitrogen was the Chilean nitrate caliche deposits, and even today no comparable source of solid nitrates is known in the world. The source of nitrates before discovery of the Chilean deposits was animal wastes. The Chilean deposits are still being exploited but production is small; in 1968, $NaNO_3$ and KNO_3 production from there was equivalent to 0.12 million tons of nitrogen (Lewis, 1970a). Nevertheless, their importance as a potential resource is large, and they supply other valuable coproducts.

Caliche layers containing nitrates are extensive in the Atacama Desert of northern Chile and are known to occur in the coastal desert of Peru as far north of Arequipa. The caliche layer is at or near the surface and generally is 3–12 feet thick. Evaporite minerals occur as cementing material in regolith (the cement commonly makes up about a third of the caliche) and as veins and impregnations in bedrock. The principal minerals are soda-niter ($NaNo_3$), halite (NaCl), and several sulfate minerals; the deposits are unique in also containing iodate minerals.

Reserves of Chilean nitrate ore containing 7 percent (present cutoff grade) or more $NaNO_3$ are estimated to be about 2.5 billion tons. Contained in this ore are an estimated 220 million tons of $NaNO_3$, 1 million tons of iodine, 9 million tons of B_2O_3, and substantial amounts of less valuable components. Caliche that is similar but contains less than 7 percent $NaNO_3$ is even more widespread in northern Chile and probable resources are more than 25 billion tons.

STRONTIUM

Strontium and its compounds are used chiefly for pyrotechnics and similar purposes that utilize the red coloration of its flame, but some is used for vacuum tubes, greases, ceramics, color television tube glass, and other purposes. In 1968, about 6,500 tons of strontium was consumed in the United States.

Most production comes from celestite ($SrSO_4$), although strontianite ($SrCO_3$) is locally abundant. Current production of strontium minerals comes chiefly from Mexico and the United Kingdom. The United States has sources of strontium, but all present consumers utilize imported ore (Park, 1971).

Bedded deposits of celestite and strontianite in California were mined during World Wars I and II. They consist of concretionary layers of the minerals in Cenozoic lacustrine deposits made up chiefly of tuff and shale. Both celestite and strontianite deposits contain gypsum and some include halite; the strontianite beds are also associated with limestone. The strontium minerals formed largely by replacement of preexisting clastic sediments, but

some may have been part of the original sediment. Deposits in 11 other States are mostly replacement, vein, disseminated, or vuggy occurrences in older rocks (Durrell, 1953; Schreck and Arundale, 1959).

Resources in the United States have been estimated at 3.5 million tons of rock containing 85 percent or more $SrSO_4$. World resources are probably many times larger. Brines containing several thousand parts per million strontium exist and might also be utilized. At present rates of consumption, the U.S. resources of celestite and strontianite represent a 500-year world supply (Schreck and Arundale, 1959; Handsman, 1970). Very little prospecting for strontium minerals have been carried out in the United States or elsewhere. An extensive program could probably increase U.S. resources fourfold.

BROMINE

Annual production of bromine in the United States is almost 400 million pounds valued at $88 million. This constitutes more than three-fourths of world production. Most bromine is used in gasoline additives although some is needed for fire extinguishers, flame retardants, and other uses (MacMillan, 1970b). Inasmuch as present consumption of bromine largely reflects its use as a gasoline additive, future consumption in the United States is uncertain. Public concern over air pollution could result in a greatly curtailed use of lead in gasolines; the use of lead creates the need for ethylene dibromide as an additive.

All U.S. production comes from brines. Five plants in Michigan and five in Arkansas use brines from deep wells; one plant in California uses brines from Searles Lake. Production of bromine from sea water ceased in 1969, but the sea provides the United States with an unlimtied resource (Olson, 1971).

Well brines that allow production mostly contain more than 1,000 parts per million bromine. Typical samples of brines from producing wells in Michigan contain 1,300–2,900 ppm bromine (White and others, 1963, table 13); California brines that allow production of bromine as a byproduct contain about 850 ppm (Bixler and Sawyer, 1957); sea water contains about 65 ppm but this can be concentrated to 1,750 ppm by solar evaporation before processing (Ver Planck, 1957).

Resources of bromine are virtually unlimited. Sea water provides a source that is almost economic today, and deep-well brines now in use are available in large volume. Bittern salts and interstitial brines in marine evaporite bodies have bromine concentrations similar to those in the best deep-well brines.

IODINE

Iodine is used primarily in the manufacture of photographic chemicals, disinfectants, and pharmaceutical preparations. During World War I, it was extracted from seaweed on the west coast of the United States. Subsequently, in this country, it was derived chiefly from oil-well brines in Louisiana and California. Present production of iodine comes chiefly from gas-well brines in the Chiba Peninsula of Japan (5,092 tons in 1969) and from nitrate ores of northern Chile (2,700 tons). Imports in 1969 from these countries, which supply most U.S. requirements, were about 2,900 tons valued at $5.7 million (Park, 1971). Annual production of iodine from brines at Midland, Mich., is probably about 150 tons (MacMillan, 1970c).

The Chilean nitrate deposits contain 200–600 ppm iodine, only part of which is recovered. Iodine occurs in the minerals lautarite ($Ca(IO_3)_2$), brüggenite ($Ca(IO_3)_2 \cdot H_2O$), and dietzeite ($Ca(IO_3)_2(CrO_4)$), and probably as a contaminant in other saline minerals of the deposits. High-iodine brines of oil fields and other deep wells are characteristically chloride brines in which the iodine occurs in concentrations ranging from 35 to 135 ppm; bromine is commonly present in similar concentrations (White and others, 1963; Collins and others, 1967).

Reserves and resources of iodine in brines and nitrate deposits currently being exploited are at least 1.5 million tons, of which the Chilean nitrate deposits account for more than 1 million tons. Potential resources in these and other iodine-rich brines are several times as large; potential resources in the United States are probably several hundred thousand tons.

CALCIUM CHLORIDE

Calcium chloride is sold as crystals and as a dense brine. Its largest single market is for highway deicing, but dust control, concrete treatment, and other uses require major amounts. About one-third of the calcium chloride produced in the United States is a synthetic byproduct of sodium carbonate derived by the Solvay process; two-thirds comes from natural brines which in 1970 were processed by five plants in Michigan and two in California. Average annual production between 1965 and 1969 from natural sources was valued at $13 million (Babcock, 1964; Lansche, 1971a).

Oil-field and other deep-well brines rich in calcium chloride are generally low in carbonate and

sulfate and high in ammonia and total solids (White and others, 1963, p. 9, tables 13, 16, 29). They come from diverse geologic settings and areas, and their origin is not clear. Lake brines with comparable compositions occur in still other environments (Smith, G. I., 1966b).

Resources of calcium chloride in the world are large and, for practical purposes, nearly inexhaustible. Production in the United States is now limited primarily to the number of wells drilled in known favorable areas, but these and new wells could almost certainly supply domestic needs for at least 100 years. Billions of tons of calcium and magnesium chloride are available from tachyhydrite bodies in Brazil and western Africa (Ivanov, 1969; Hite, 1972; Wardlaw, 1972). This amount represents thousands of years supply at present world consumption rates.

MAGNESIUM COMPOUNDS

Magnesium and its compounds are produced from bedrock deposits, natural and synthetic brines, and sea water. The principal minerals mined for their magnesia (MgO) content are magnesite ($MgCO_3$), brucite ($Mg(OH)_2$), and dolomite ($MgCa(CO_3)_2$); deposits of these minerals are discussed in "Magnesian Refractories" and "Limestone and Dolomite." Most of the domestic and world production consists of magnesium metal or one of several grades of magnesia, although some is in the form of magnesium hydroxide, magnesium sulfate, magnesium trisilicate, and magnesium chloride. Magnesium metal is used extensively in aircraft manufacturing and other purposes for which its light weight is a factor, and magnesia is used chiefly as a refactory for the steel and other basic industries (Comstock, 1963; Lewis and Cammarota, 1971; Paone, 1970).

Many industrialized nations produce magnesium and magnesia from the sea that borders them. In the United States, magnesium and its compounds were produced in 1970 from deep-well brines in Michigan and from sea water in five States. The deep-well brines in Michigan supplied most of production. Facilities for extraction of magnesium compounds from Great Salt Lake brines are being constructed. Extraction of magnesium from sea water or brine also requires calcined limestone or dolomite, the latter yielding magnesium in quantities about equal to that from sea water.

The geologic environments of the raw materials used in this industry are extremely diverse. Dolomite and magnesite occur widely and were deposited in a variety of environments. Magnesium in usable concentrations is found in many surface and subsurface brines that are dominated by sulfate or chloride anions and that are deficient in carbonate. Evaporite deposits containing billions of tons of tachyhydrite ($2MgCl_2 \cdot CaCl_2 \cdot 12H_2O$) in Brazil and western Africa represent possible magnesium resources (Ivanov, 1969; Hite, 1972; Wardlaw, 1972). For practical purposes, the U.S. and world resources of magnesium and magnesium compounds in brines and sea water are unlimited, and bedrock resources are large.

UNDISCOVERED RESOURCES OF EVAPORITES AND BRINES

MARINE EVAPORITES

The ultimate supply of commodities derived from marine evaporites is theoretically limited only by the existing volume of such deposits. That volume is huge. Deposits of marine evaporites tend to be hundreds of feet thick, and Kozary, Dunlap, and Humphrey (1968) showed that about 25 percent of the world's continental area is underlain by one or more of them.

This known area of evaporites may be nearly all the total area that exists. This surprising conclusion stems from the fact that the area climatically favorable for the formation of marine evaporites at any given time in the earth's history is limited; calculations based on these limits plus reasonable geologic assumptions as to areas that might also by physiographically favorable allow one to approximate the maximum area of evaporites that could have formed since the close of Precambrian time. One such calculation, described below, shows that maximum area to be about 60 percent of the earth's surface. However, after subtracting areas representing reasonable guesses of the area of nondeposition and loss due to erosion, the remainder barely accounts for the evaporite bodies now known. Less conservative, but still reasonable, assumptions fail to account for all known deposits. Alternative models are virtually limited to those that increase the depositional area, and experimentation has shown that geologically reasonable alternatives that make substantial differences in the conclusion are difficult to find. For this reason, the conclusion regarding the small number of undiscovered evaporite bodies seems sound and not likely to be wrong by any factor approaching an order of magnitude. A more detailed explanation of calculating procedures and assumptions follows.

Virtually all marine evaporites apparently formed where warm arid climates prevailed along coasts or in large embayments connected with the sea.

Warm and arid coastal regions today are mostly in the zones of trade winds (zones of nearly constant wind direction) that lie between about 10° and 35°, both north and south of the equator. The arid coasts are where the trade winds blow from the land toward the sea. At least since Precambrian time, trade-wind belts probably have had about the same size and global distribution; they are products of the interaction between solar energy and the spinning earth and its atmosphere, and it is reasonable to postulate that the output of solar energy, the earth's spin and the physical properties of the atmosphere have been nearly constant during that period. These 25°-wide trade-wind belts make up about 40 percent of the global surface. If one assumes that two landmasses lay astride these belts, each with a 5°-wide (about 300 miles) evaporite-forming basin along the entire shoreline that is in the trade-wind belt, about 1 percent of the globe would be accumulating evaporites. If, in the geologic past, the number of continental landmasses astride the trade-wind belts averaged two, and if the configurations of the coastlines changed every 10 million years sufficiently for new portions of the earth's surface to begin accumulating evaporites, there could have been as many as 60 different accumulations of this size in the 600 million years since the close of Precambrian time. This means that about 45 percent of the globe could have at one time been the site of evaporite deposition.

This maximum possible area does not seem to be large enough. Considering the near absence of present-day evaporite-forming basins, it seem likely that on the average, far less than half of the climatically favorable sites in the past were likely to be occupied by basins that produced evaporites. Furthermore, very probably at least half of once-formed evaporites have been eroded or dissolved. Finally, one must consider that the area of known evaporites would substantially exceed 8 percent of the earth's surface if none of the evaporite deposits overlapped. Conceivably, other environments than those considered in this model have produced major quantities of marine evaporites, but available geologic evidence seems more consistent with this model than any other. For these reasons, the numbers used in the above model calculation probably could be changed substantially and still not account for the known areas of marine evaporite deposits. Numbers and assumptions that would lead to the conclusion that areas of undiscovered evaporites are large would require even more drastic departures from what seems geologically reasonable.

The only alternative assumption that seems to be reasonable for this calculation is that the areas of accumulating evaporites were commonly much larger than postulated because in some respects, past environments differed intrinsically from those of the present. It is difficulty to envision larger areas of global aridity caused by wider trade-wind belts, but very possibly areas of inland seas were much larger than now known. Available evidence indicates that many of the world's present continental areas were originally part of a single landmass and that the present continents evolved by the slow spreading of individual masses away from this center. As they spread, nearly landlocked inland seas may have evolved to become sites of evaporite deposition that were much larger than any now known. Such a phenomenon could explain the apparent overabundance of marine evaporite bodies, but still does not necessarily imply that a large number of evaporite bodies are undiscovered.

If one accepts the above lines of reasoning, it follows that the likelihood of finding many large new deposits of marine evaporites is small. This means that estimates of resources in known deposits can be considered nearly equivalent to ultimate resources. An estimate of these figures follows. If 25 percent of the world's 57 million square miles of continental area is underlain by evaporite deposits, and the average deposit contains 300 feet of evaporites, 0.8 million cubic miles of evaporites exist. (The average of the maximum thickness of deposits listed in table 42 is 750 feet; the deposits are estimated to contain 20 percent impurity and to have average thicknesses that are half their maximum thickness.) An independent estimate of this volume by Ronov (1968, fig. 3) concludes that approximately 0.9 million cubic miles of evaporites are in the earth's sedimentary shell, with about 70 percent of this volume in relatively near-surface deposits formed in platform environments and the remainder formed in geosynclinal environments. Most evaporites consist of gypsum, anhydrite, or halite; thus, a volume of 0.8 million cubic miles means that about 10^{16} tons of these components exist.

An estimate by us (based on well-explored portions of U.S. deposits) suggests that about 0.002 percent of an average marine deposit consists of potassium mineral concentrations, although this has to be a very approximate number. Applying this figure to the 0.8 million cubic miles of evaporites in the world suggests that about 160 billion tons of KCl containing 100 billion tons of K_2O is concentrated in such bodies. This is very close to the amount inferred to exist in known deposits and

tends to support the inference that most of the earth's evaporite and potash deposits have already been discovered. No doubt some deposits remain unknown, but the above calculation strongly implies that the number is not large.

In the United States, all marine evaporite deposits represent possible sources of potassium compounds, salt, and gypsum. Figure 24 shows that about 35 percent of the 3 million square miles that make up the 48 adjoining States is underlain by evaporites, and calculations like those used for estimating world resources indicate that about 8 billion tons of K_2O equivalent could be contained in these deposits. This amount is about 20 times greater than estimates of known U.S. resources and suggests that several large undiscovered deposits may exist.

In summary, it is not likely in the foreseeable future that potassium compounds, salt, or gypsum will become the sole target of expensive exploration programs because of dwindling world supplies. Enormous quantities are now known although their global distribution is uneven. However, there is strong incentive to keep costs of these substances low because their costs influence the price of a very large number of other products. Furthermore, strategic reasons, balance of payment problems, differences in quality of the product from different sources, and potential profits stemming from attractively priced transportation to large or growing markets remain as strong incentives for exploration. New and exploitable resources may well be discovered as a result of these stimuli.

NONMARINE EVAPORITES

Ultimate resources of commodities derived from continental evaporites—deposits formed by the evaporation of inland bodies of water—are less easily evaluated than are resources of marine evaporites. Requirements for an environment favorable for the deposition of continental evaporites are a semiarid to arid climate that will produce a high evaporation rate, a closed basin having internal drainage, and a source of large quantities of water having the proper ratio of dissolved components. Evaporation rates high enough to keep closed basins from filling and overflowing exist today in areas that mostly lie between lats 45° N. and 45° S.; the sizes and locations of basins within such areas, however, are variable. Closed basins receive large inflow where they adjoin high mountains or upland areas; the high mountains or uplands extract most of the moisture from passing airmasses, and the closed basins downwind from the mountains are arid because they have been deprived of this moisture. Extensive faulting and warping are the geological processes required to create both the basins and the mountains.

Areas known to contain large volumes of nonmarine sedimentary rocks that were deposited in closed basins between the 45° parallels represent a subordinate part of the world's surface. Most known continental evaporite deposits are Cenozoic, and some evaporite assemblages are favored by drainage from a volcanic rock environment whereas others are favored by drainage from other types of terrane; these factors provide further guidance to areas that should be considered during exploration for deposits and in estimating undiscovered resources.

In the United States, virtually all areas that have had a long history of internal drainage are west of the Rocky Mountains, although several basins having more brief histories of interior drainage lie in the Great Plains. In the area between the Wasatch Range and the Sierra Nevada, more than 100 closed basins are large enough to have contained lakes during the Pleistocene, and probably 5–10 times this number of closed basins existed during one part or another of Cenozoic time. Between 500 and 1,000 such basins may therefore have formed in that area, and the sediments deposited in perhaps half are now preserved. Of these basins, less than 10 percent have been adequately prospected. If remaining basins were tested and a 1-percent success [1] resulted, two to five basins would be found to contain evaporite deposits. Although such deposits might be profitable, the degree of increase to resources would depend on the minerals they contain; salt, potash, sodium carbonate, or magnesium deposits would probably not greatly change the resource outlook, but deposits containing other possible components might. Discovery of new deposits in favorable areas in other parts of the world is even more likely because these parts have been less explored; western China and adjacent parts of Afghanistan and the U.S.S.R., Iran, Turkey, western Central and South America, and eastern Africa all have probably had Cenozoic geologic histories similar to the Western United States. If those areas together contain 10 times as many basins as the Western United States, it seems likely that 20–50 major deposits of continental

[1] A basis used by some mining companies for budgeting mineral exploration programs in geologically favorable areas is to spend up to 1 percent of the value of the anticipated ore body. This figure is commonly justified by citing past experience, which sbows that there is about a 10 percent chance of success in finding an ore body that would allow at least a 10 percent profit. The 1 percent chance of success used in the present calculation results from an estimate that only 10 percent of the basins in this area are geologically favorab'e, and that 10 percent of them—1 percent of the total number—would contain a deposit.

evaporites remain to be discovered in the world. These might increase world resources of their components by 1 to 2 orders of magnitude above resources in known deposits.

BRINES

Sea water, lakes, seas, and many shallow subsurface brines have known compositions. They are not, therefore, "undiscovered," but they do represent potential resources because processes capable of extracting selected dissolved components at a profit may someday be developed. Those bodies contain large to virtually unlimited quantities of several commodities. New extraction processes for many substances are not likely to be developed out of world necessity inasmuch as known reserves and resources appear adequate for hundreds or thousands of years. Some may be developed, however, as new techniques allow some chemicals to be extracted more cheaply or closer to markets.

Deep subsurface brines contain very large quantities of dissolved substances, but few basins outside of known or potential petroleum and gas fields have been explored. The geologic factors controlling the distribution of valuable brines are not well understood and the number of unexplored basins containing valuable brines cannot be reliably estimated. In some areas, the amount of brine now extracted is controlled by petroleum production. More could be extracted if necessary, but the quantity cannot be evaluated although it is known to be large.

SUMMARY OF U.S. RESOURCES

Evaporite resources of the United States, expressed as years supply at current rates of consumption are shown in table 43. Although known domestic resources of potassium compounds are relatively low, Canadian resources are sufficient to fulfill requirements of North America for thousands of years.

PROBLEMS FOR RESEARCH

The abundance of evaporite and brine resources means that no shortage is impending. Continuing effort should be made toward finding new and more economic deposits, however, because they would supply large quantities of the basic chemicals required in industry and agriculture, and their cost would be an important factor in the price consumers pay for many products. For this reason it is imperative to have not only resources, but resources that would permit these chemicals to be produced and transported to the consumer at low cost. The main problems posed by resources derived from evaporites and brines are that the costs of some are undesirably high today and costs of others are likely to increase in the future. These problems are results of the uneven geographic distribution of deposits throughout the United States and the world, and the increasingly low-grade ores and the more complex and expensive extraction processes needed to utilize them. Discovery of new and more inexpensively processed deposits is needed. The abundance of known deposits of marine evaporites minimizes the need to find new ones, and efforts should be concentrated on locating the more valuable concentrations of minerals within the known deposits. In contrast, a large percentage of the world's deposits of nonmarine evaporites and brines are undiscovered, and extensive programs of geologic study and drilling will be needed to find them.

Important to the geologic understanding of evaporite and brine deposits are a knowledge of (1) the variations in past positions of global climatic belts, (2) the times of past fluctuations in global climatic character, (3) the processes involved in the concentration and crystallization of evaporite components from waters, and (4) the mechanics of diagenesis that affect solids and brines both immediately and long after burial. Major obstacles to the finding and development of new evaporite resources stem from our imperfect understanding of these phenomena, and research leading to an improved understanding is essential.

TABLE 43.—*Evaporite and brine resources of the United States*

[Expressed as years supply at current rates of domestic consumption]

Commodity	Identified resources [1] (Reserves [2] and subeconomic deposits)	Undiscovered resources (Hypothetical [3] and speculative [4] resources)
Potassium compounds	100 years	Virtually inexhaustible.
Salt	1,000+ years	Do.
Gypsum and anhydrite	500+ years	Do.
Sodium carbonate	6,000 years	5,000 years.
Sodium sulfate	700 years	2,000 years.
Borates	300 years	1,000 years.
Nitrates	Unlimited (air).	Unlimited (air).
Strontium	500 years	2,000 years.
Bromine	Unlimited (sea water).	Unlimited (sea water).
Iodine	100 years	500 years.
Calcium chloride	100+ years	1,000+ years.
Magnesium	Unlimited (sea water).	Unlimited (sea water).

[1] Identified resources: Specific, identified mineral deposits that may or may not be evaluated as to extent and grade, and whose contained minerals may or may not be profitably recoverable with existing technology and economic conditions.

[2] Reserves: Identified deposits from which minerals can be extracted profitably with existing technology and under present economic conditions.

[3] Hypothetical resources: Undiscovered mineral deposits, whether of recoverable or subeconomic grade, that are geologically predictable as existing in known districts.

[4] Speculative resources: Undiscovered mineral deposits, whether of recoverable or subeconomic grade, that may exist in unknown districts or in unrecognized or unconventional form.

Almost every subdivision of earth sciences has contributed techniques useful in prospecting for evaporites. It is, in fact, this variety in disciplines that makes it difficult for exploration groups to utilize known techniques effectively because so few groups include members that have facility in all fields. All subdivisions of the sciences also have great promise of developing new techniques. New geochemical methods, for example, may well enhance our ability to reconstruct salinity gradients within evaporite-bearing basins. Variations in the bromine content in halite of marine origin provide an established technique, but far less work has been done on the distribution of other elements that reflect salinity as they change concentration in minerals associated with evaporite bodies. Such changes might be indicated by variations in the concentration of strontium as it proxies for calcium in minerals such as limestone, dolomite, gypsum, and anhydrite; by shifts in the isotopic ratios of both hydrogen and oxygen in the water of liquid inclusions which may reflect changes in evaporation-induced salinity of crystallizing brines; or by variations in the O^{18} in the sulfate ion of gypsum and anhydrite which may change during evaporation of the parent brine yet be less affected by diagenesis than most other ions or radical components.

Also needed are more complete studies of evaporite deposits in the process of being formed. Few marine deposits are forming today, and none has been examined in all ways that are desirable. More nonmarine deposits than marine are being formed today, and immediate studies of many are needed because these evaporites may not repeat their depositional cycle.

Perhaps the least understood geologic phenomena related to evaporites and brines are the roles and mechanisms of diagenesis. Almost immediately after deposition, some changes in mineral composition and form occur that stem from changes in the surrounding chemical and physical conditions relative to those extant at the site of original crystallization. Other changes occur later—for example, as deeper burial increases load pressures, as tectonic and other forces alter the hydraulic regimes that control the migration of interstitial brines, as time allows metastable assemblages of minerals to convert to thermodynamically stable assemblages, and as clay, organic, and other substances that act as ionic filters change the compositions of brines passing through them. Field studies of these problems have been made, but progress is difficult because so much of the evidence has been destroyed or is not available from existing drill cores. Laboratory studies are difficult because so many of the reactions are slow. Future research should be more fruitful because the problems are becoming better defined and new techniques are becoming available, but much remains to be done.

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FELDSPAR

By Frank G. Lesure

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ABSTRACT OF CONCLUSIONS

Feldspar is the general name for an important group of aluminum silicate minerals used primarily in the glass and ceramic industries. Although consumption in the United States has more than doubled since 1940, domestic reserves and resources are considered adequate for anticipated demand. Transportation costs are a major factor in the delivered price of feldspar and contribute to the use of substitutes where available. Research problems involve identifying potential sources nearer to consumers. Demand for feldspar in the United States by the year 2000 is expected to be three to five times present production. This demand is in large part based on the increasing use of container glass and will depend partly on the recycling of bottle glass and the continued increase in the use of throwaway bottles.

INTRODUCTION

Feldspar is the general name for a group of anhydrous aluminum silicate minerals that contain varying amounts of potassium, sodium, and calcium. The feldspars are important rock-forming minerals and constitute nearly 60 percent of many igneous rocks. The principal potassium feldspars, orthoclase and microcline, have the same chemical composition ($KAlSi_3O_8$), but different crystal forms. The sodium-calcium feldspars, called plagioclase, form a complete series of minerals ranging from pure $NaAlSi_3O_8$ (albite) to pure $CaAl_2Si_3O_8$ (anorthite). The plagioclase minerals between albite and anorthite in order of decreasing sodium content and increasing calcium content are oligoclase, andesine, labradorite, and bytownite. Most natural orthoclase and microcline contain 10–25 percent $NaAlSi_3O_8$, and most plagioclase contains 5–15 percent $KAlSi_3O_8$. Intergrowths of orthoclase or microcline with albite are called perthite and they are a common constituent of pegmatites.

Producers and consumers know feldspar as a beneficiated mixture composed of feldspar minerals with ideally less than 5 percent but sometimes as much as 20 percent of quartz, and minor quantities of other minerals. Perthitic microcline (potash spar), albite (soda spar), and oligoclase (soda-lime spar) are the principal types of feldspar mined in the United States.

USE AND ECONOMIC IMPORTANCE

From 1955 to 1970, about 55 percent of the feldspar sold in the United States was used in glass, 31 percent in pottery, 4 percent in enamel, and 10 percent in soaps, abrasives, mineral fillers, welding-rod coatings, and other miscellaneous uses. Feldspar is a source of alumina, soda, and potash for glass. The alumina improves workability, retards devitrification, and increases the chemical stability of the finished product. Iron oxide, a coloring agent, is the most common undesirable impurity in glass-grade feldspars. The maximum acceptable iron-oxide content of feldspar for flint glass is 0.1 percent, but as much as 0.5 percent is acceptable for green or amber glass. Minerals too refractory to melt at tempera-

tures used in glass manufacture are undesirable impurities because unmelted fragments appear as flaws in finished glass. Specifications for most glass manufacture require the feldspar to be ground to minus 20 or 30 mesh and not more than 10–20 percent to be ground to minus 140 mesh. Minor amounts of feldspar were used in glass as early as 1895 but its use in container glass was generally adopted by major producers in 1924 and became standard industry practice about 1935. Use of feldspar in the flat-glass industry was standard by 1940. A little more than 110 pounds of feldspar is used in an average ton of glass containers and slightly less than 100 pounds in a ton of flat glass.

Feldspar is useful in ceramic batches because it fuses at lower temperatures than most of the other ingredients, and as a result, it cements crystalline phases in some types of ceramic bodies and acts as a flux in physicochemical reactions of crystalline phases in whiteware. The feldspar, which imparts strength, toughness, and durability to the finished product, makes up 10–35 percent of the body and 30–50 percent of the glaze in many types of ceramics. The ratio of potash to soda in the feldspar affects the firing characteristics, and in general, high-potash material is preferred. Feldspar products are available with potash-to-soda ratios varying from 5 to 1 to less than 1 to 1. A maximum iron-oxide content of 0.1 percent, specified limit for silica, and absence of dark mineral particles are also required. Feldspar for most ceramic use is ground to minus 200 mesh. It has been used as a separate ingredient in ceramics in China since the Tang dynasty (A.D. 621–945) and in Europe since the 18th century (Burgess, 1949, p. 349).

Uses of feldspar other than in glass and ceramics are few, and consumption is small, but use as a mineral filler, especially in latex, is growing. The most important other uses are in abrasives and scouring soaps because of physical properties such as cleavage, hardness, and white color. Excellent cleavage in two directions provides sharp edges; but feldspar hardness, being less than that of glass, minimizes damage to glass and glazed whiteware by scratching. Feldspar is also used in electric welding-rod coatings as a source of potassium to improve arc characteristics and to serve as a flux. It has been used in roofing granules and poultry grit and for other crushed-stone uses.

In recent years, various materials have been used in the glass and ceramic industries as substitutes for feldspar. Chief among these are nepheline syenite, aplite, talc, pyrophyllite, electric furnace slag, and lithospar. Most nepheline syenites contain too much iron oxide for use in glass, but a deposit in Ontario, Canada, that is low in iron is mined extensively for this purpose. "Aplite" in the glass trade is the name for a mixture of plagioclase and microcline produced in Amherst and Nelson Counties, Va., by flotation methods from anorthosite. Talc replaces feldspar in dinnerware and wall tile; pyrophyllite is used instead of feldspar in enamels and wall tile. Electric-furnace slag is used as a substitute source of alumina for glass, and lithospar is a naturally occurring mixture of spodumene and feldspar used as a flux.

The United States is or could be self-sufficient in feldspar production. In 1970 we imported 3,247 long tons, mostly from Canada, and exported about 5,000 long tons. Reserves are large, and until recently the industry operated at only 50-percent capacity. Less than 1 percent of the feldspar used in the United States is imported, but large amounts of nepheline syenite, as a substitute for feldspar in glass and ceramics, are imported from Canada. These shipments began in 1936, and in recent years they have increased more rapidly than domestic feldspar production (fig. 25). The U.S. production of feldspar

FIGURE 25.—Crude feldspar sold or used by producers in the United States, 1900–1970, compared with imports of nepheline syenite 1937–1970. Derivation of domestic feldspar is shown for 1955–70. Data from U.S. Geol. Survey and U.S. Bur. Mines, Mineral Resources of the U.S. and Minerals Yearbook, 1900–70.

was about 28 percent of the estimated world production in 1970 (Wells, 1972, p. 2).

Principal production of feldspar in the rest of the world in 1970 is in Europe, close to large markets for glass and ceramics. Major producers are West Germany, the Soviet Union, Italy, France and Norway; smaller production came from Finland, Spain, Yugoslavia, Poland, Sweden, and Portugal. In Africa, the major producers are the Republic of South Africa and Ethiopia; in Asia, Japan, the Philippines, India, and Korea; in the Western Hemisphere, Mexico, Argentina, and Colombia.

The forecast demand for feldspar in the United States in the year 2000, based on a projected growth rate of gross national product, is 2–3 million tons (Cooper and Wells, 1970, p. 983). Demand for feldspar will fluctuate mostly with demand for glass containers, flat glass, and pottery. If a significant amount of bottle glass is recycled or if the use of throwaway bottles decreases, feldspar needs will decrease.

EXPLOITATION

Feldspar was first mined in the United States in 1825. The mineral came from pegmatite bodies in Connecticut and was shipped to England for use in ceramics (DuBois, 1940, p. 207). Principal production from 1853 to 1910 was from Connecticut, New York, Maine, Pennsylvania, and Maryland. Although there is a legend that the Indians mined and sold semikaolinized feldspar from western North Carolina before 1744, the first recorded shipment from that State was made in 1911. Within several years North Carolina became a major producer of feldspar and has for many years accounted for at least half of the annual U.S. production. In recent years California, Connecticut, South Carolina, Georgia, and South Dakota have been our other important feldspar producers. Production fluctuates from year to year, but it has in general steadily increased since 1940, when use of feldspar in glass became common (fig. 25).

Most of the feldspar produced in the United States until 1946 consisted primarily of perthite and oligoclase hand-cobbed from coarse-grained pegmatites. In 1936, the U.S. Bureau of Mines began an investigation of the concentration of feldspar by table agglomeration and flotation (O'Meara and others, 1939). The first commercial plant to produce feldspar for glass by flotation began operation at Kona, Mitchell County, N.C., in 1946. Use of flotation permitted low-cost mining of finer grained pegmatite and granite and expanded the potential sources of raw material. Quartz and flake mica are commonly byproducts of flotation feldspar. Some flotation feldspar is also produced as a coproduct in the mining of lithium-rich pegmatites, especially in North Carolina. Recent studies by the U.S. Bureau of Mines and others have shown the practicability of producing feldspar, quartz, and mica concentrates from granitic rocks (Hill and others, 1969) and of utilizing tailings from feldspar plants in North Carolina (Redeker, 1970).

In 1970, about 57 percent of the feldspar used in the United States was taken from flotation concentrates, 8 percent was hand sorted, and 35 percent was from feldspar-silica mixtures (Wells, 1972, p. 2). In 1955, these figures were 40, 45, and 15 percent, respectively (fig. 25).

Feldspar is mined by open-pit and underground methods. Most of the mines producing ore for beneficiation are open pits using power equipment and yielding 300–800 tons per day. Selective mining is done in zoned pegmatites, usually at a rate of less than 100 tons a day. The broken rock is sorted by hand during loading or on a picking belt. Feldspar has also been produced as a byproduct of sheet-mica mining, which requires the broken rock to be sorted and moved by hand. The number of small producers using hand-cobbing methods is decreasing as labor and material costs increase; in 1971, only four mills in the United States were using hand-cobbed ore. Details of the mining, beneficiation, and marketing of feldspar are given by Castle and Gillson (1960), Cooper and Wells (1970), and Feitler (1967).

The average price of crude feldspar per long ton was $14.87 in 1970 and $9.51 in 1960 (Wells, 1972, p. 2). The average price of ground feldspar per short ton was $14.60 in 1970 and $13.40 in 1960. Prices quoted for ground feldspar for December 1970 were as follows: North Carolina 20 mesh, flotation, $11.00; 200 mesh, flotation, $20.50–$26.00 (Engineering and Mining Journal, 1970).

Transportation cost is an important element in marketing feldspar for glass because the delivered cost per unit of alumina plus alkalies is the basis for determining relative value of competing feldspar products. Nepheline syenite from Canada has an advantage over feldspar from Southern United States in the glass markets of parts of New York, New Jersey, Pennsylvania, and Ohio because of its greater content of alumina plus alkalies and because of more favorable freight rates. The ceramic industry, however, is more concerned with a particular feldspar and its effect on the delicate balance of ceramic mix, plant operation, and product quality. In general, one feldspar product cannot be substituted for another in a ceramic mix without extensive tests. A ceramic feldspar is sometimes shipped past

another producing plant to a consumer who would rather pay more freight than change suppliers.

Environmental problems of feldspar mining are standard for a nonmetallic mineral mined by open-pit methods. Large dumps may be avoided by better coproduct or byproduct recovery, especially of quartz sand, mica, or feldspar-silica mixtures. Dust hazards also can be avoided. Some open pits may be utilized for lakes or reservoirs; the impounded water should generally be clear because sources of feldspar usually lack sulfide minerals that produce acid mine waters.

GEOLOGIC OCCURRENCE

Commercial deposits of feldspar are found in some pegmatites, many granites and related igneous rocks, and certain beach sands and alluvium. Most pegmatites are light-colored coarsely crystalline igneous rocks, which are found as lenticular or tabular bodies in metamorphic rocks or in large granitic intrusions. Individual mineral grains and crystals range in length from less than 1 inch to many feet. Pegmatite bodies vary in size from small pods and veins to large masses hundreds of feet thick and thousands of feet long. Feldspar, quartz, and mica are the most common minerals present, but many rare and unusual minerals are found in some deposits. In many pegmatite bodies the minerals are somewhat evenly distributed throughout, but in others the minerals are segregated into certain layers or parts of the body, called zones. These zones can sometimes be selectively mined to recover the desired minerals by hand sorting and are, therefore, important economically. Most of the feldspar produced in the United States before 1946 was perthite, which commonly is abundant as very large crystals in the intermediate zones or cores of zoned pegmatite bodies.

The principal pegmatite districts in the United States are in New England, especially Maine, New Hampshire, and Connecticut, in the Appalachian Piedmont from Virginia to Alabama, and in the Blue Ridge Mountains in North Carolina and Georgia. Smaller districts are in the Black Hills of South Dakota, the Front Range of Colorado, several areas in northern New Mexico, western Arizona, and southern California; minor districts are in Nevada, Montana, Wyoming, Idaho, and Washington (Cameron and others, 1949; Jahns, 1955).

Granite and related igneous rocks are composed of one or two kinds of alkalic feldspar; quartz; and minor amounts of various other minerals, mainly muscovite, biotite, hornblende, or rarely pyroxene. Feldspar content ranges from 50 to 70 percent, and grain size from less than one-fourth inch to about an inch. Deposits range from small masses measured in feet to very large masses measured in miles. Granitic rocks such as alaskite, that contain only small amounts of ferromagnesian minerals, locally are mined in bulk and a mixture of potassium and sodium feldspar recovered by milling and flotation. Mixtures of feldspar and quartz are also produced as byproducts of granite quarrying.

Granites are common igneous rocks that occur widely in the crystalline terranes of the world. Large granitic bodies in the United States are scattered throughout New England; the older Appalachians from New York to Alabama; the Llano area, Texas; northern Wisconsin and adjacent Michigan; northern Minnesota; the St. Francois Mountains, Mo.; the Black Hills of South Dakota; the Rocky Mountains from New Mexico to Wyoming; and in isolated mountain ranges of Arizona, Utah, and Nevada. Large batholithic intrusions are in California, Idaho, Montana, and Washington.

Feldspathic beach sands and alluvial deposits may be rich enough to be mined for their feldspar content. The dune sands of Pacific Grove, Monterey County, Calif., which have been worked extensively, contain about 53 percent quartz, 46 percent feldspar, and less than 1 percent other minerals in an area about 6 miles long and 1 mile wide. Alluvial deposits along the Mississippi, Illinois, Wabash, and Ohio Rivers and dune and beach sands of Pleistocene age in Illinois contain 5–25 percent feldspar, 2–12 percent feldspathic rock fragments, 60–80 percent quartz, and some chert and heavy minerals. The alluvial sands are in low river terraces, in present channels, and in sandbars (Hunter, 1965). Similar deposits along the Kansas, Arkansas, Little Arkansas and Republican Rivers in Kansas contain as much as 27 percent feldspar.

Authigenic potash feldspar has been reported from many sedimentary rocks of various lithologies and ages (Sheppard and Gude, 1965, p. 6). Feldspar content may range from less than 10 percent in some shales and siltstones to as much as 90 percent in some tuffaceous beds. Recent work on Cenozoic tuffs in saline lake beds in California, Oregon, Nevada, and Arizona has shown a definite zonal pattern to these deposits (Sheppard and Gude, 1968; Sheppard and Walker, 1969). At the margins of former lakes, most of the tuff beds contain unaltered glass and grade into a zeolite facies toward the middle of the lakes; however, near the centers of the lakes in areas of higher salinity nearly pure beds of potash feldspar are found. The deposits studied to date contain more iron and are finer-grained than is desired for glass feldspar. The tuff beds, however, are 2–8 feet thick and may cover tens of square

miles and so significant tonnages of nearly pure potash feldspar may be present in California in the Barstow Formation of Miocene Age, San Bernardino County, and in Lake Tecopa, Inyo County (Sheppard and Gude, 1965, 1968).

RESOURCES

IDENTIFIED AND HYPOTHETICAL RESOURCES

Identified and hypothetical resources of feldspar in the United States are large enough to meet any anticipated demand, but quantitative data are not available for calculations on reserves. A recent estimate by the Bureau of Mines (Cooper and Wells, 1970, p. 985) of our feldspar reserves is 500 million long tons of material similar to that being mined in 1970. Reserves in the Spruce Pine district of North Carolina alone exceed 200 million tons of material within 50 feet of the surface (Brobst, 1962, p. A15). Immense hypothetical resources of feldspar exist in granitic rocks exposed in the igneous and metamorphic terranes of the United States and many other countries. Although almost any granite can be used, those that contain few ferromagnesian minerals, such as the alaskite of Spruce Pine, N.C., are the most satisfactory. The average granite body is generally thousands of feet to several miles wide and may contain 60 percent or more feldspar plus potential byproduct quartz and flake mica.

Reserves and resources of feldspar in pegmatites are difficult to estimate. Many deposits of high-grade potash feldspar in zoned pegmatites have been worked out, but most of these were in pegmatite bodies exposed at the surface. It is safe to assume that the present surface is a random sample of what exists at shallow depths, less than 500 feet, and therefore our undiscovered resources of feldspar in zoned pegmatites not exposed but within minable depth are equal to the amount already mined, that is, more than 8 million tons. Prospecting for these deposits will not be easy, but detailed geologic mapping, geophysical techniques, drilling, and possibly geochemical methods can be used. Because of the availability of resources of fine-grained feldspar and the low prices of crude ore, the additional expense in exploring for more zoned pegmatites is probably not justified at this time.

Domestic and foreign reserves and resources of feldspar in feldspathic sands are also large. Such deposits may contain from 20 to at least 50 percent feldspar, at least 50 percent quartz, and only minor amounts of other minerals. Deposits may cover many acres or even square miles. Unlike nearly all other mineral deposits, alluvial sands dredged from stream channels are renewable. Such deposits are becoming more desirable, not only because they can be mined inexpensively, but also because they can be used as feldspar-silica mixtures with very little beneficiation. A few deposits of this type have been studied and several are being mined, but many more probably exist. Recent mapping by the U.S. Geological Survey in southern Delaware and adjacent Maryland has outlined a large outcrop area of the Beaverdam Sand, a feldspathic marine sand of Pleistocene age (J.P. Owens, written commun., 1972). Preliminary studies indicate a feldspar content as high as 50 percent of equal amounts of plagioclase and microcline. The sand has a known thickness of 80–90 feet and is exposed in an area of about 1,800 square miles.

Resources of authigenic feldspar are very large, but until further study is made of the uses of such material, these deposits are only a potential resource.

SPECULATIVE RESOURCES

Identified and hypothetical resources of feldspar are so large that little thought has been given to speculative resources. The basic types of igneous feldspar deposits, the coarse-grained feldspar in pegmatite and the finer grained in granite, occur in igneous and metamorphic terranes, most of which are probably identified in much of the world. A few additional districts may be found in areas not yet mapped. The distribution of detrital and authigenic feldspar in sediments is not so well known, and the possibility of discovery of new districts is probably greater than for the igneous deposits. Speculative resources of both types are probably large, but prospecting and resource study will be concentrated more on the known districts or in areas nearest to markets because of the high cost of transportation and the low value of the commodity.

PROBLEMS FOR RESEARCH

Even though existing sources of feldspar are large, continued evaluation of potential sources should be made during regional geologic mapping. Because transportation costs make up a major part of the delivered cost of feldspar, the most pressing need in the United States is for discovery of supplies closer to consuming areas, especially in the Central States. Possible sources in that area—in feldspathic sands and granites—have been outlined, but additional work is needed on technical feasibility, economic evaluation of markets, and byproduct recovery. Geologic mapping may outline additional or more economic sources in the Central States.

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FLUORINE

By R. G. Worl, R. E. Van Alstine, and D. R. Shawe

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ABSTRACT OF CONCLUSIONS

Fluorine is used by industry mainly as fluorspar (CaF_2) for flux in steel making; as synthetic cryolite (Na_3AlF_6) and aluminum fluoride in the manufacture of aluminum metal; and as fluorocarbons in refrigerants, aerosol propellants, solvents, and many other compounds. Fluorine consumption in the United States and the world has increased greatly since World War II, while fluorine production in the United States has remained static. The United States produces only 20 percent of its requirement at the present.

Fluorine in nature is dominantly in the combined form and tends to concentrate in specific geologic environments. Preferred igneous associations are silicic and alkalic extrusives and intrusives, complex pegmatites, carbonatites, and contact aureoles of these. Sedimentary rocks containing concentrations of fluorine are volcaniclastic, lacustrine, evaporite, marine carbonate, and marine phosphorite beds. Major concentrations of fluorine occur in hydrothermal fluorspar deposits. Hydrothermal deposits are distributed among a wide variety of geologic environments in the form of veins, mantos, stratiform beds, pipes, stockworks, and alteration zones.

Commercial sources of fluorine to date have been dominantly hydrothermal deposits of fluorspar. Additional sources in the future will be as byproducts from ores of other commodities, as coproducts of multicommodity ores, and from fluorine deposits other than hydrothermal. A major future source of fluorine will be as a byproduct of the processing of phosphate rock, because fluorapatite ($Ca_5(PO_4,CO_3)_3F$) is the major component of phosphate rock.

World reserves of fluorspar (50 percent CaF_2) are estimated to be 190 million short tons, of which 25 million are in the United States. Speculative resources of fluorine in the world are probably very large.

INTRODUCTION

Fluorine, a versatile element, is widely used in many industries and will probably remain in great demand in the future. Present and potential sources of fluorine are the major fluorine-bearing minerals fluorite, cryolite, fluorapatite, and topaz. In this report attention will be given mainly to fluorspar, the ore of the mineral fluorite, until recently virtually the only commercial source of fluorine. Synthetic cryolite now has commercial value, but with minor exceptions, other fluorine-bearing minerals have not had commercial value.

Fluorspar is marketed in three grades; acid, ceramic, and metallurgical (Hodge, 1971, p. 10). Acid-grade fluorspar contains a minimum of 97 percent CaF_2 and a maximum of 1.5 percent SiO_2. Limits are commonly placed on other common impurities—$CaCO_3$, sulfide sulfur or total sulfur, iron, lead, zinc, and phosphorus. Ceramic-grade fluorspar

varies according to consumer demands but generally contains 85–96 percent CaF_2 and has limits on SiO_2, $CaCO_3$, Fe_2O_3, sulfide sulfur, lead, and zinc. Metallurgical-grade fluorspar (metspar) is commonly listed in market quotations as 60, 70, and 72.5 effective CaF_2 units; effective CaF_2 unit is a measure obtained by multiplying the SiO_2 content of the ore by 2.5 and subtracting this figure from the CaF_2 content of the ore. Specifications for metspar usually set maximum limits of 0.3 percent sulfide sulfur and 0.25–0.5 percent lead. Consumers desire metspar in the form of lumps or gravel having no fines and a maximum size of about 2 inches. Pellets and briquets made from fines and flotation concentrates are now replacing lump and gravel metspar in the United States. It is significant from an economic standpoint that metspar is used virtually as it occurs in nature, fluorite (CaF_2) plus impurities.

Fluorspar as a flux in steel making accounts for 33 percent of the U.S. fluorine demand; fluorspar as an iron foundry flux, a nonferrous metals flux, and an additive in electrometallurgy accounts for 8 percent. Several possible substitutes for fluorspar in steel fluxing have been tried, including calcium chloride, bauxite and colemanite (hydrated borate of calcium). None of these appears to be usable on a large scale, but a concentrated effort is being made by the steel industry to develop a usable synthetic flux.

Cryolite (Na_3AlF_6) and synthetic aluminum fluoride are essential in the manufacture of aluminum metal. Most cryolite used is synthetic and is made by combining caustic soda, alumina, and hydrofluoric acid, or is prepared from waste solutions containing 15–25 percent fluosilicic acid recovered in manufacture of superphosphate.

Natural or synthetic cryolite is the major flux used in reducing alumina to aluminum metal in electrolytic cells, and this use accounted for about 18 percent of the U.S. fluorine demand in 1968. Not all the fluorine is lost in this process, and progress is being made in recovering some of the fluorine volatilized or wasted. This practice may reduce slightly the acid-grade fluorspar requirement from the present 135 pounds per ton of aluminum produced. The use of lithium carbonate as an additive in aluminum manufacture also seems to reduce the fluorine consumption.

Fluorine consumed in the United States is mainly in the form of fluorspar, 44 percent; hydrofluoric acid (fluorocarbons), 35 percent; hydrofluoric acid (cryolite), 18 percent; and fluosilicates, 3 percent (MacMillan, 1970, p. 993). The production of fluorocarbon compounds has only recently reached its present consumption level and will probably remain a major consumer of fluorine for some time. Fluorocarbon compounds are used in many ways—refrigerants, aerosol propellants, solvents, and special-use plastics—and demand for fluorine is expanding rapidly as new uses of these unique compounds are developed. Fluorocarbons conceivably could be replaced in part by liquid nitrogen and compressed gaseous nitrogen, which are readily available now as byproducts of liquid-oxygen production. Fluorine used in the ceramic, glass, welding-rod, and enamel industries constituted about 6 percent of the U.S. fluorine demand in 1968.

In 1970 the United States accounted for about 6 percent of the world's production of fluorspar but consumed 30 percent of this production. Thus in that year the United States produced only 20 percent of the fluorspar it consumed; the other 80 percent was imported mainly from Mexico, Spain, and Italy. In the recent past the United States produced only 15 percent of its consumption of fluorine; the 1970 increase probably reflects in part the release by the U.S. Government of large amounts of stockpiled acid-grade fluorspar.

EXPLOITATION

Until recently, fluorspar was virtually the only source of fluorine, and it will probably remain the major source in the near future. A relatively minor amount of the fluorine consumed is at present being recovered from the processing of phosphate rock, which, along with other byproduct and coproduct sources, will become increasingly important in the future. Though data are not readily available, the amounts of byproducts recovered from fluorspar mining in the past apparently were not significant. Sulfide concentrates—mainly lead, zinc, and silver—are recovered in some operations, and barite is recovered as a coproduct in a few operations.

Since World War II (fig. 26) world fluorspar production and U.S. fluorspar consumption have increased greatly, whereas U.S. production has remained nearly static. The great increase in fluorspar consumption reflects the worldwide increased production of steel and aluminum and the utilization of fluorocarbons in many new industries.

GEOLOGIC ENVIRONMENT

GEOCHEMISTRY

Fluorine (atomic number 9, atomic weight 19) consists of a single isotope occurring in nature mostly as a singly charged anion, F^-, but also occasionally as a compound of complex anions, such as $(BF_4)^-$. Fluorine is a gaseous element, and large

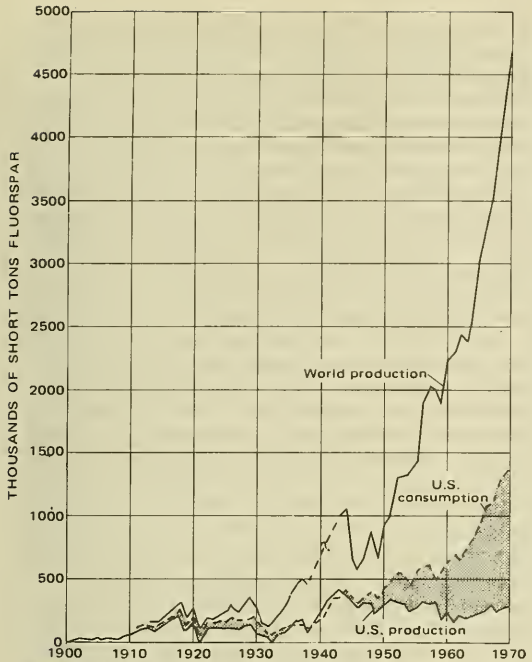

FIGURE 26.—World production, 1913–70, U.S. production, 1900–70, and U.S. consumption, 1911–70, of fluorspar (CaF_2).

amounts of gaseous fluorine are given off in some active volcanic areas. Most fluorine in nature, however, is found combined in solid form. The radius of the fluoride ion F^- (1.33 A) is very close to that of the hydroxyl ion $(OH)^-$ (1.33 A) and the oxygen ion O^{-2} (1.32 A), and with proper valence conditions, diadochic substitution of F^- for $(OH)^-$ or O^{-2} is relatively simple. Fluorine in the lithosphere therefore is tied up as an essential element in fluoride minerals or as a substitute in other minerals, mainly silicates and phosphates. Fluorite, CaF_2, is geologically the most abundant and economically the most important fluoride. Some other fluorides of possible economic significance are cryolite, Na_3AlF_6; sellaite, MgF_2; villiaumite, NaF; and bastnaesite, $(Ce,La)(CO_3)F$, whereas other, still less common fluorides will probably be of little economic significance in the future. Fluorine occurs in many silicate minerals, including tourmaline, topaz, and the micas phlogopite, zinnwaldite, lepidolite and biotite, and in the phosphates monazite, xenotime, fluorapatite, and amblygonite. Fluorapatite, $Ca_5(PO_4,CO_3)_3F$, and topaz, $Al_2SiO_4(F,OH)_2$, are of economic significance.

The organic chemistry of fluorine in terms of fluorosis and fluorocarbons is well understood; the geochemistry of fluorine is not. The distribution of fluorine in the earth's crust can be noted but not adequately explained. Crustal abundance is difficult to determine. Fleischer and Robinson (1963, p. 67) reported a value of 650 ppm (parts per million) fluorine for the average content of the continental rocks of the earth's crust. They also gave the following mean values, in parts per million, for various rock types: basalt, 360; andesite, 210; rhyolite, 480; phonolite, 930; gabbro and diabase, 420; granite and granodiorite, 870; alkalic rocks, 1,000; limestone, 220; dolomite, 260; sandstone and graywacke, 180; shale, 800; oceanic sediment, 730; and soil, 285. The geochemical cycle of fluorine and the problems associated with fluorine determinations were discussed by Fleischer and Robinson (1963) and Barth (1947).

Although fluorine is widespread throughout the lithosphere, biosphere, and hydrosphere, it tends to be concentrated in fairly specific environments. In igneous activity fluorine is considered as a characteristic component of the volatile phase of magmatic differentiation. More specifically fluorine is concentrated in alkalic and silicic hypabyssal and extrusive rocks and related hydrothermal deposits, in complex pegmatites, in carbonatites, and in alteration zones, including greisens, associated with alkalic, silicic and carbonatite intrusive rocks. Fluorine becomes concentrated in sedimentary environments largely by precipitation as fluorite, other fluorides, or fluorapatite during accumulation of the sediments or during their subsequent diagenesis. These minerals are not common as detrital components of the rocks. Five general groups of sedimentary deposits contain concentrations of fluorine: volcaniclastic, lacustrine, evaporite, marine carbonate, and marine phosphate beds.

Fluorine is a common but variable constituent of gases and waters of volcanic origin, mainly as HF but also as F_2, SiF_4, and H_2SiF_6. Volcanic exhalations contribute large quantities of fluorine to the surface environment. For example, Zies (1929) estimated that at one time the Valley of Ten Thousand Smokes, Alaska, was releasing HF at the rate of 200,000 tons annually.

The fluoride content of ground water ranges from zero to a maximum recorded value of 67.2 ppm, and few waters contain more than 10 ppm. Large areas of the world, however, locally have ground waters containing more than 1.5 ppm F. The fluoride content of ground water depends in part upon the nature of the bedrock. Alkalic igneous rocks, dolo-

mites, phosphorites, and, especially, volcanic glass give rise to high fluoride waters.

Surface waters vary greatly in fluoride content depending upon source of the water and amount of rainfall, the fluoride content generally being higher in dry periods. Fleischer and Robinson (1963) gave 0.2 ppm as the average fluoride content of rivers. This figure also is probably close to that for freshwater lakes. Highly saline lakes, on the other hand, have much higher fluoride contents: 14 ppm is reported for Great Salt Lake, Utah, and as much as 1,627 ppm for lakes in Kenya.

Individual species of plants contain variable quantities of fluorine depending upon the amounts they need for growth and the amounts available in the soil or air. Some plants can be classed as fluorine accumulators, and some plants increase in fluorine content with age. Other plants accumulate fluorine from the air only. All these factors must be considered if fluorine in plants is to be used in exploration for ore deposits.

Fluorine deposits of past and present significance, of probable future significance, and of possible future significance are classified into the following four groups, which, although they overlap and intergrade somewhat, provide a convenient basis for further discussion.

1. Fluorine deposits associated with igneous rocks. Includes disseminated deposits, deposits in pegmatite and carbonatite, and deposits in contact aureoles.
2. Fluorine deposits associated with sedimentary rocks. Includes those in volcaniclastic and lacustrine sedimentary rocks and those in evaporite, marine carbonate, and phosphorite rocks.
3. Fluorine deposits associated with regionally metamorphosed rocks.
4. Fluorine in hydrothermal (hot water) deposits. Includes those in veins and mantos, in pipes and stockworks, and in zones of alteration.

FLUORINE DEPOSITS ASSOCIATED WITH IGNEOUS ROCKS

Fluorine deposits associated with igneous rocks contain fluorine minerals that are considered to be genetically related to the igneous rocks. These deposits include accessory fluorine minerals disseminated through the igneous rock and fluorine minerals in pegmatites, carbonatites, and contact aureoles of intrusive rocks. Fluorine-bearing igneous rocks of possible future economic significance are hypabyssal bodies and extrusive rocks, generally of alkalic or silicic-alkalic composition, and plutonic rocks of silicic composition. Topaz and fluorite occur in some silicic volcanic rocks of the Western United States (Shawe, 1966, p. C209), where they are dispersed through the rock and concentrated within vugs. Stocks of alkalic rocks in the Western United States and in many other parts of the world contain fluorite and, in places, topaz as accessory minerals. Fluorite also is a common constituent of batholithic rocks of granite composition in South Africa, Newfoundland (Van Alstine, 1944), the United States, Eastern Mongolia (Khasin and Kalenov, 1965), and many other parts of the world. Although large amounts of fluorine occur in these rocks, the tenor is low, generally less than 2 percent CaF_2.

Some pegmatites and carbonatites are mined for their fluorine content. Pegmatites commonly contain local concentrations of fluorite and other fluorides, but not in large volume. Most fluorite mined from pegmatites has been used as specimens or for optical purposes. However, the fluorspar deposits at Crystal Mountain, Mont., and the cryolite deposits at Ivigtut, Greenland, are both considered to be almost monomineralic pegmatites. The Crystal Mountain deposits are mainly fluorite but have minor amounts of biotite, quartz, feldspar, sphene, rare-earth-bearing apatite, amphibole, fergusonite, thorianite, and thortveitite (Parker and Havens, 1963). This deposit is exceedingly rich and has yielded a substantial amount of fluorspar since production began in 1952. The deposit at Ivigtut, Greenland, is largely cryolite but also contains complex fluorides, fluorite, microcline, topaz, columbite, siderite, sphalerite, galena, and chalcopyrite.

Carbonatite complexes are notably enriched in fluorine, which is mostly dispersed through the rock in silicates and apatite. Economic fluorine deposits associated with carbonatite complexes are contact-zone deposits and late-stage hydrothermal veins. Deposits at Okorusu in South West Africa and at Amba Dongar, India, are of this type (Deans and others, 1972). Apatite-bearing carbonatite rock is the principal source of phosphate in southern and eastern Africa. The apatite rocks, of which there are considerable reserves, contain 1–3 percent fluorine (Deans, 1966, p. 393). Apatite-bearing carbonatite rock near Jacupiranga, São Paulo, Brazil, being mined for phosphate, contains 4–5 percent fluorine (Abreu, 1960, p. 123), and apatite-bearing carbonatite rocks in the U.S.S.R. are a present source of fluorine; the fluorine is recovered as a byproduct of fertilizer production. Carbonatite at Mountain Pass, Calif., contains at least 1 percent fluorine, mostly in bastnaesite (Olson and others, 1954).

Fluorite, topaz, and apatite are common minerals in contact aureoles around many intrusive bodies,

mainly silicic and alkalic rocks and carbonatite complexes. The fluorine minerals occur in tactite and in posttactite hydrothermal veins and replacement bodies. Contact-zone fluorspar deposits, mined in Korea and Japan, are generally small podlike bodies about 20 meters long, 10–15 meters wide, and 10 meters high. The deposits in Korea are replacement bodies in limestone at the contact with younger "granites" and are of two types: a low-temperature type consisting mainly of fluorite, quartz, and coarsely crystalline calcite, and a high-temperature type consisting of epidote and calc-silicates in addition to fluorite, quartz, and calcite (Gallagher, 1963, p. 93). Both types contain some sulfides.

Fluorspar deposits associated with the Okorusu complex in South West Africa are veins and replacement bodies in the contact aureole of carbonatite intrusives. At Amba Dongar, India, the main economic concentrations of fluorite occur as veins and replacement bodies in carbonate wallrock around late-stage ankeritic carbonatite intrusives which are also fluorite-bearing (Deans and others, 1972, p. B6). Fine-grained cherty quartz and minor amounts of barite, dickite, galena, pyrite, and chalcopyrite are associated with fluorite at Amba Dongar. Metasomatic phlogopite rocks around carbonatite plugs in Zambia, Malawi, and Rhodesia contain anomalous amounts of fluorine. The fluorine in these dull-gray rocks is contained largely in fluor-phlogopite, but some occurs in sellaite (Deans and others, 1972, p. B6).

FLUORINE DEPOSITS ASSOCIATED WITH SEDIMENTARY ROCKS

Some fluorine deposits in sedimentary rocks appear to be genetically related to the enclosing sediments, but some of the deposits may be of hydrothermal or metasomatic origin. They occur in volcaniclastic sedimentary rocks; lacustrine deposits; and evaporite, marine-carbonate, and marine-phosphate rocks. Fluorine minerals generally do not occur in detrital accumulations of economic value.

Although volcanic ash commonly contains fluorine in glass shards and absorbed on tephra, commercial or potential deposits of fluorine in volcaniclastic sedimentary rocks seem to be either disseminated deposits of probable hydrothermal origin or interbedded deposits of lacustrine origin. Fluorite-beryllium deposits in altered volcaniclastic sedimentary rocks near Spor Mountain, Utah, described later in this chapter, are considered to be of hydrothermal origin. Fluorspar deposits near Rome, Italy, and Rome, Oreg., are lacustrine deposits interbedded with volcaniclastic sedimentary rocks.

Fluorspar deposits in unconsolidated tuffs near Rome, Italy, are lenses composed of finely crystalline fluorite, barite, calcite, dolomite, apatite, opal, and chalcedonic quartz and minor amounts of detrital minerals and volcanic glass. The fluorite content of some zones averages 55 percent. These lenses are thought to be sedimentary deposits of chemical origin formed in lake basins that were subject to emanations of hydrothermal fluids rich in fluorine, calcium, barium, strontium, silicon, sulfur, and phosphorus (Spada, 1969).

Near Rome, Oreg., fluorite occurs as submicroscopic, nearly spherical grains in tuff, tuffaceous mudstone, and mudstone of Tertiary lacustrine deposits. Fluorite content is generally less than 5 percent but is as much as 16 percent in some zones. According to Sheppard and Gude (1969, p. D69) the "fluorite probably formed during diagenesis in sediments that had been deposited in an alkaline, saline lake."

Some lacustrine brines and evaporites contain concentrations of fluorine; the best examples are the brines and recent evaporites of lakes in the rift valleys of Africa, where lake waters contain as much as 1,627 ppm fluorine. The evaporite sequence of Lake Magadi, Kenya, composed largely of trona, locally contains as much as 22 percent villiaumite (NaF), and fluorite is common throughout much of the sequence (Sheppard and Gude, 1969, p. D73).

In the U.S.S.R., possible economic concentrations of fluorine in marine carbonates and evaporites of the Permian Preurals have been noted (Abramovich and Nechayev, 1960). Fluorite occurs as a fine dissemination and as crystalline aggregates in vugs in dolomitized limestone. The CaF_2 content of some zones exceeds 30 percent. In the United States a minor occurrence in Permian dolomitic limestones of the Rocky Mountains contains 12–15 percent CaF_2. In marine carbonates of the U.S.S.R., as noted by Kazakov and Sokolova (1950), fluorite is related to the saline facies of relict basins, mainly to dolomite, dolomitized limestones, gypsum, redrocks, anhydrite, potassium and magnesium salts, and celestite. According to them (p. 68 of the English translation) the fluorite was precipitated from sea water that had been concentrated three to four times, and continued to precipitate from the brine in a dying sea basin where potassium salts and borates were being deposited.

The ore mineral of sedimentary phosphate rock is carbonate fluorapatite with ratio of F to P_2O_5 about 1 to 10. Phosphate rock contains as much as 4 percent F and 40 percent P_2O_5, although lower grade deposits are now mined for their phosphate content.

Plants in eight countries are recovering fluorine as a byproduct (Wood, 1972). The fluorine in phosphate rock could have been part of the original precipitate, or, inasmuch as calcium phosphate or calcium hydroxy-phosphate can collect fluorine from very dilute solutions, it could have been introduced later. (See also the chapter in this volume entitled "Phosphates.")

FLUORINE DEPOSITS ASSOCIATED WITH METAMORPHIC ROCKS

Topaz and tourmaline are common in metamorphic rocks and may represent future sources of fluorine. For example, a Precambrian topaz-quartz-sillimanite gneiss in the central part of the Front Range, Colo., contains major amounts of topaz (Sheridan and others, 1968). This unit, part of a high-grade metamorphic gneiss and granitic plutonic complex, is 11–100 feet thick and crops out along strike for 7,000 feet. Three composite chip samples of this unit were found to contain 67, 23, and 36 weight percent topaz and 4.2, 3.9, and 2.2 weight percent rutile. The gneiss may warrant investigation as an ore of rutile, especially since it might also yield topaz or topaz and sillimanite as byproducts (Sheridan and others, 1968).

FLUORINE IN HYDROTHERMAL DEPOSITS

Historically, the dominant commercial sources of fluorine have been fluorspar deposits of hydrothermal origin. Hydrothermal fluorspar occurs in a wide variety of types of deposits formed in many geologic environments under a wide range of physical-chemical conditions. Fluorite is generally the only fluorine mineral in these deposits, and its abundance ranges from nearly 100 percent down to trace amounts. Other common minerals are quartz, chalcedonic quartz, opal, barite, manganese oxides, calcite, clay minerals, and lead and zinc sulfides. The following elements are commonly, but not universally, present in these deposits, and at many places they are in trace amounts only: silver, gold, beryllium, iron, manganese, molybdenum, lead, the rare earths, tin, tellurium, uranium, vanadium, tungsten, and zinc (Worl, 1971). Hydrothermal fluorite occurs in almost any type of host rock but especially in carbonate, silicic igneous, and silicic metamorphic rocks.

The form of hydrothermal fluorspar deposits is the standard basis for their classification. Most common forms are veins and mantos, which are abundant in well-defined regions of the world. Individual veins range in thickness from millimeters to several meters and are as much as several kilometers in length. Fluorspar mantos, or blanketlike replacements of rock, are generally confined to marine carbonate rocks and commonly extend outward from veins. Mantos are irregular lenticular or wedge-shaped bodies and are not layered concordantly within a stratigraphic sequence. Fluorspar in many veins and mantos is characterized by monomineralic banding, crustification, and mammillary textures. Massive crystalline material, breccias, and fine-grained earthy material are also common. Most fluorspar veins and mantos contain at least 35 percent CaF_2; many contain at least 70 percent CaF_2; and some contain as much as 98 percent CaF_2.

Although host-rock compositions were important in localizing many individual deposits, regional structures controlled the location of most hydrothermal fluorspar districts. Fluorite veins and mantos in many areas are confined to large faults and subordinate fissures of deep-seated regional tensional nature, as in India (Deans and others, 1972), in Eastern Mongolia (Khasin and Kalenov, 1965), in the Western United States (Worl, 1971), and along the rift valleys of Africa. Regional domes and arches helped localize fluorspar mineralization in the Illinois-Kentucky district of the United States (Heyl and Brock, 1961) and in the North Pennine ore field of the United Kingdom (Sawkins, 1966). Hydrothermal fluorspar veins and mantos have been documented all over the world, some of the best known occurring in Mexico (Van Alstine, 1961), the United States (Grogan and Bradbury, 1968), Spain (Marin and deLis, 1945), Brazil (Abreu, 1960), South Africa (DeKun, 1965), the U.S.S.R. (U.S. Bur. Mines, 1958), Korea (Gallagher, 1963), Canada (Van Alstine, 1944), Italy (Spada, 1969), France (Chermette, 1960), Pakistan (Bakr, 1965), and Thailand (Gardner and Smith, 1965).

Some districts characterized by veins and mantos contain individual hydrothermal fluorspar deposits best described as stockworks and pipelike bodies. Fluorspar pipes mined in the Thomas Range, Utah, and near Beatty, Nev., are circular to elliptical in plan and range in diameter from 5 to about 45 meters (Peters, 1958, p. 672). Much of the fluorspar at Jamestown, Colo., and the Buffalo mine, Union of South Africa (DeKun, 1965, p. 409), is in the form of stockworks of veins and veinlets. Fluorspar pipes and stockworks commonly occur at fault intersections and are generally associated with stocks and hypabyssal bodies of igneous rock. Fluorspar production from Jamestown, Colo., has been from breccias containing 50–90 percent CaF_2 within the stockwork. Fluorspar in stockworks generally is diffused through large bodies of rock so that the ore grade is

low, but the reserves may be substantial.

In the Western United States many areas of hydrothermally altered volcanic rock, agglomerates, volcaniclastic sediments, and unconsolidated clastic sediments contain dispersed fluorite. The fluorite-beryllium deposits near Spor Mountain, Utah, and the Honey Comb Hills, Utah, are good examples (McAnulty and Levinson, 1964). Altered water-laid tuff near Spor Mountain, Utah, contains commercial amounts of beryllium and about 4 percent CaF_2. Microscopic fluorite occurs dispersed through altered tuff and in a fine-grained intergrowth with opal and chalcedony in nodules as much as 30 centimeters in diameter. Part of the fluorite in these deposits probably represents redeposition of fluorine leached from the included volcanic ash. However, much of the fluorine, along with beryllium, gallium, lead, lithium, niobium, cesium, and yttrium, seems to have been introduced with laterally spreading hydrothermal solutions (Staatz and Griffitts, 1961; D. A. Lindsey, oral commun., 1972).

Hydrothermal fluorspar deposits in general formed under a wide range of conditions, from high pressure and temperature at depth to low pressure and temperature near the surface, and were precipitated from solutions of varied chemical composition. Nevertheless, each individual deposit formed under a relatively small range of conditions. Fluorite at the Tyrny-Auz skarn complex, North Caucasus, U.S.S.R., formed from pneumatolytic and hydrothermal solutions at temperatures in excess of 500° C. The initial hydrothermal solutions were highly supercharged with chlorides and fluorides of sodium, potassium, calcium, and other elements (Lesnyak, 1965, p. 484). At Jamestown, Colo., fluorite in a stockwork next to an alkalic intrusive formed from solutions that varied in composition with time and space. The main-stage fluids were highly saline (26–32 percent equivalent NaCl) and near 350°C, though the fluids at times were alternately supersaline, CO_2 rich, or relatively dilute and cool (J. T. Nash and C. G. Cunningham, oral commun., 1972). Fluorite in veins not closely associated with igneous rocks in southern New Mexico formed from solutions that changed with time. As the temperature decreased from about 200°C to about 140°C over several substages of deposition, the salinity increased from about 10 percent equivalent NaCl to about 15 percent equivalent NaCl (Roedder and others, 1968, p. 336). Fluorite in banded and crustified epithermal veins, common throughout the world, formed from very dilute solutions at temperatures ranging from 50° to 200°C (Ermakov, 1965, p. 197; Steven, 1960, p. 410). The nature of near-surface fluorite deposits, such as at Spor Mountain, Utah, suggests that the fluorite must have been deposited from very dilute and low-temperature (50°–100°C) solutions. Stratiform lead-zinc-fluorine-barium deposits of the English Pennines and the Illinois-Kentucky district were formed from relatively high-salinity solutions (20 percent equivalent NaCl) at temperatures ranging from 75° to 200°C (Sawkins, 1966, p. 385).

Many fluorine deposits can be attributed to late stages of igneous activity. The solutions depositing the fluorine in many places seem to have had a common source with the magmas that formed related fluorine-bearing igneous bodies and carbonatite complexes. The common source was probably a differentiating magma deep in the crust or a zone of fractionation in the upper mantle. The partitioning of fluorine between the hydrothermal solutions and the late siliceous magma must have been nearly equal.

The source of the ore-forming solutions for some fluorine deposits, such as the stratiform deposits of the English Pennines and the Illinois-Kentucky district, is much debated. Most workers agree that these deposits formed from slow-moving, relatively hot (75°–200°C), dense, sodium-calcium-chlorine-fluorine brines containing abundant organic matter. Davidson (1966) suggested that the brines were derived from the diagenesis of overlying evaporites and that they concentrated their metals from the limestone and other rocks traversed. Dunham (1966), pointing to the low sodium/potassium ratios of the brines, as little as 6:1, compared with 39:1 for normal sea water, suggested that the relative enrichment in potassium appears to rule out purely connate solutions as the source of the brines. He preferred nonevaporitic connate water, reinforced by juvenile fluids associated with an igneous heat source below, as the origin of ore-forming brines. Grogan and Bradbury (1968) suggested that the brines were magmatic, connate, and meteoric in origin, and that the fluorine and metals were of magmatic origin.

Probably in most fluorine deposits the materials making up the ore-forming solution came from more than one source. The ultimate source of the fluorine needed to form the deposits is generally unknown; the relationship of fluorine deposits to major structures points to a deep-seated origin. Still, the regional distribution of fluorine in the Western United States through geologic time suggests that once a specific region becomes enriched in fluorine, it remains so through several geologic cycles and episodes of mineralization (Peters, 1958, p. 685).

RESOURCES

IDENTIFIED AND HYPOTHETICAL RESOURCES

Fluorspar deposits, although generally small, are relatively abundant and widespread throughout the world. The world's known reserves are adequate to meet the current demand, especially as fluorspar prices rise; improved mining and processing techniques have increased reserves substantially over earlier estimates. The beneficiation of fluorite-barite ores, now profitable in the United States, United Kingdom, Italy, Spain, and Tunisia, has extended world reserves. Fluorspar is currently one of the most sought-after industrial minerals, and deposits continue to be discovered in many countries. The most recently found deposits are chiefly in the United States, Mexico, Argentina, Brazil, United Kingdom, France, Spain, Italy, Thailand, India, and southern Africa.

Fluorspar resources are chiefly in shallow, low-temperature, hydrothermal vein, pipe, and manto or stratiform deposits; however, an increasingly important source of fluorspar will be as a coproduct of mining and processing certain ores of iron, lead, zinc, bismuth, tungsten, molybdenum, tin, beryllium, and rare earths that contain fluorite as a minor constituent. In the United States it is now profitable to mine ores containing as little as 15–20 percent CaF_2 if they have sufficient lead or zinc values to compensate for the low fluorite content. Molybdenum deposits of the Western United States, such as at Questa, N. Mex., contain fluorite; and although the percentage is small, the large tonnages of rock processed may warrant extraction of fluorite. Contact replacement iron-ore deposits in the Iron Springs district, Iron County, Utah, contain fluorapatite. Although the fluorine content is less than 1 percent, fluorine is being extracted during processing of this ore for its iron content. Environmental considerations in the future, in fact, may demand the recovery of fluorine during ore processing so that it is not released into surficial material, the atmosphere, or surface waters. More and more fluorspar will be recovered elsewhere from mine dumps and tailings resulting from the working of some metalliferous deposits, as is now being done in Mexico, the United Kingdom, and Spain.

The estimate of the world's resources of fluorspar ore in table 44 is based largely on published information. The figures are rounded, but they indicate orders of magnitude. This new total for the estimated fluorspar resources of the world, 190 million tons, agrees well with recent estimates of 150 million tons by Chermette (1968) and 182 million tons by the U.S. Bureau of Mines (Wood, 1972). Each of the two countries with the largest resources of fluorspar, Mexico and the United States, has about 25 million tons.

TABLE 44.—*Estimated fluorspar resources of the world*

[Millions of short tons of crude ore. The ratio of crude fluorspar ore to processed fluorspar recovered is about 3:1]

Area	Identified resources [1]	Hypothetical resources [2]
United States	25	45
Mexico	25	50
Canada	10	15
Europe [3]	62	84
Africa [4]	39	310
Asia [5]	25	62
South America [6]	3	6
Australia	1	1
Total	190	573

[1] Chiefly exploitable economic ore containing 35 percent or more CaF_2 or equivalent in combined fluorspar and metal values. The average CaF_2 content is about 50 percent. Includes some subeconomic material.
[2] Some material of ore grade, but much rock is exploitable only under more favorable economic or technologic conditions. Deposits incompletely known, because few subeconomic fluorspar deposits have been explored.
[3] Chiefly France, Germany, Italy, Spain, United Kingdom, and U.S.S.R.
[4] Chiefly Kenya, Morocco, Mozambique, Rhodesia, South West Africa, Tunisia, and Union of South Africa.
[5] Chiefly China, India, Korea, and Thailand.
[6] Chiefly Argentina and Brazil.

A previous detailed reserve estimate (Van Alstine, 1956) for fluorspar deposits of the United States showed 22.5 million tons of commercial ore and about 12 million tons of lower grade material containing 15–35 percent CaF_2. As a result of mining and discoveries since 1956, the identified resources in the United States are now estimated at about 25 million tons, largely in Illinois, Kentucky, Texas, New Mexico, Nevada, Utah, Colorado, Idaho, Montana, and Alaska. Nearly all of this resource is believed amenable to processing into acid- and metallurgical-grade products, the latter grade especially by pelletizing flotation concentrates.

As European fluorspar consumption continues to increase, the substantial exports from Italy and Spain to the United States probably will not be available. This situation should make the mining of even more low-grade resources profitable and should stimulate further domestic exploration. Detailed information is lacking on which to base accurate estimates of hypothetical resources of most low-grade fluorspar deposits in foreign countries.

Marine phosphate rock, by far the world's largest fluorine resource, generally contains about 3 percent fluorine. Resources of phosphate rock in the United States are chiefly in Florida, North Carolina, Tennessee, Utah, Wyoming, Idaho, and Montana. Reserves there are about 10 billion tons of phosphate rock, and hypothetical resources have been estimated at more than 60 billion tons; the latter class represents a potential fluorine resource of about 2 billion tons and is equivalent to about 4 billion tons of

fluorspar. Similar deposits of phosphate rock, with estimated reserves totaling more than 10 billion tons and enormous hypothetical resources, occur mainly in Morocco, Tunisia, Algeria, Turkey, U.S.S.R., Peru, China, North Vietnam, and Australia. Potentially several hundred thousand tons of fluorine annually could be obtained as a byproduct of phosphate production in the United States. The estimated quantity of fluorine discarded or lost during the processing of phosphate rock in the United States approximates the annual fluorspar imports into the United States (Blake and others, 1971). In recent years more than 100,000 tons of hydrofluosilicic acid was recovered in the United States during the manufacture of superphosphates and was used mostly for water fluoridation; however, some of this acid is now processed further into aluminum fluoride and synthetic cryolite for the aluminum industry and into fluosilicates. Fluorine from phosphate rock for the aluminum industry will become more competitive with fluorspar in the next few years, as fluorspar prices rise, as the demand grows, and as the phosphate industry strives to control environmental pollution near processing plants by recovering the fluorine. Industrial plants in the United States, Mexico, Canada, U.S.S.R., Austria, Rumania, India, and Japan now use waste hydrofluosilicic acid from the processing of phosphate rock, and other plants are planned for France, West Germany, Switzerland, and Australia. (See also the chapter on "Phosphate Deposits" in this volume.)

Topaz, although rarely concentrated, occurs in probable commercial quantity and grade in at least two localities in the United States. At the old Brewer gold mine in South Carolina, reserves were estimated at about 100,000 tons of schist averaging approximately 15 percent topaz and about 1,200 tons of topaz in adjacent placer deposits that contain 1–24 percent topaz. The hypothetical resources at this deposit are estimated at about 800,000 tons of ore. In the Front Range, Colo., a lens in Precambrian gneiss containing about 15 percent topaz was estimated to constitute a reserve of about 600,000 tons of topaz-bearing rock. The hypothetical resources of this topaz-bearing rock are estimated to be about 250,000 tons for every 100 feet of depth.

Bastnaesite in carbonatite at Mountain Pass, Calif., is a potential resource of fluorine. This rare-earth mineral contains about 7 percent fluorine and constitutes 5–15 percent of the carbonatite rock. On the basis of an estimated 100 million tons of potential ore at Mountain Pass (Olson and others, 1954), about 1 million tons of fluorine is estimated as a potential byproduct of rare-earth extraction.

SPECULATIVE RESOURCES

Exploration for and evaluation of fluorine resources must be based upon the geology and geochemistry of fluorine. The important geologic parameters are regional tensional faults or other deep-seated structures, alkalic and silicic igneous rocks, carbonatites, and hydrothermal activity—including hot springs. Fluorine is apparently very mobile in geologic settings characterized by these parameters, and in addition to forming deposits directly related to those features, it also has moved into other geologic environments associated in time and space to form deposits there. For example, fluorine mobilized by exhalations or weathering has been transferred from the alkalic igneous rocks and carbonatites along the African rift structures into the lake brines, to be concentrated in evaporites of the rift valleys. Fluorine-bearing solutions genetically related to the important geologic parameters have permeated country rock, such as the altered and mineralized volcaniclastic sedimentary rocks of the Western United States; have replaced receptive country rocks, as in the Illinois-Kentucky district; and have filled subsidiary fractures, in places some distance from the igneous activity and major structures, as in many smaller fluorspar districts of the Western United States.

The important geologic parameters listed above define environments and processes in which fluorine was available in abnormal amounts in some part of the system and in which it could be mobilized and transported into concentrations of economic interest. Geologic processes in other environments also have acted to concentrate minor amounts of fluorine (of the order of crustal abundance) into deposits of economic interest, as in the precipitation of fluorapatite from sea water.

These principles assure us that numerous possibilities exist for the discovery of new resources of fluorine. The best possibilities are undiscovered but geologically predictable fluorine districts; known small, but high grade, deposits; and very large low-grade multicommodity ores. At this time it is impossible to give a quantitative indication of speculative resources, other than that they are probably very large.

In the United States new fluorspar districts might be found northwest of the important Illinois-Kentucky district in carbonate rocks beneath the cover of Pennsylvanian rocks, and also northeast of this district toward Ohio and the Michigan basin beneath Pleistocene cover where fluorite occurrences are known in Silurian and Devonian dolomites. Similarly the Paleozoic carbonate rocks of central Tennes-

see and Kentucky are widely mineralized with fluorite, as shown in recent drilling, and may contain other commercial deposits. Large, but lower grade, stratiform fluorspar deposits in carbonate rocks, like those worked in the United States, France, U.S.S.R., and southern Africa, probably will be popular targets for exploration. In the Western United States fluorspar deposits undoubtedly underlie parts of the widespread cover of Tertiary and Quarternary sedimentary and volcanic rocks. Cenozoic tuffaceous lake beds in the Western United States, Italy, and southern Africa contain fluorite, some of commercial interest, and other occurrences of this type of fine-grained fluorite may have been overlooked. Some fluorspar deposits of the Western United States are related genetically to areas of silicic volcanic rocks, namely the Big Bend subprovince of Texas; the Nacimiento subprovince of Arizona, New Mexico, and Colorado; and the Shoshone province of Nevada, Utah, Idaho, and Montana. Other areas with relatively high fluorine content in volcanic rocks might be worthy of further prospecting, especially southeastern Idaho, northwestern Wyoming, and northwestern Utah. In west-central Utah, topaz is disseminated in volcanic rocks, and commercial fluorspar deposits are distributed around the southern and western periphery of a caldera. Only a third of the caldera is exposed; the remainder, which is covered by rhyolite flows or alluvium, may contain undiscovered deposits (Shawe, 1972, p. B76–B77). A tectonic unit consisting of the Rio Grande trough in New Mexico, and its northern extension through Colorado, Wyoming, and Montana, is especially rich in fluorspar deposits and should be explored further. Deposits of syngenetic fluorite associated with gypsum and limestone are reported from Permian marine evaporites in the Big Horn Mountains, Wyo.; similar extensive deposits are known in the Permian of U.S.S.R., and other equivalent evaporites should be investigated for deposits of fluorite.

Large deposits of fluorapatite in marine phosphate rock probably exist beneath the sea in Tertiary coastal plain sediments extending east from deposits in North and South Carolina and Florida. Fluorine is recovered from huge deposits of fluorapatite in alkalic rocks of U.S.S.R., and other deposits of this type may be found and profitably explored elsewhere.

Probably millions of tons of topaz-bearing rock are yet to be discovered in widespread metamorphic terranes throughout the world. Because cryolite, Na_3AlF_6, is a rare mineral, it probably will not be an important source of fluorine; the world's only known commercial deposit of natural cryolite, in Greenland, has been depleted. Sodium fluoride has been found in saline lake beds in Tanganyika and may some day be a source of fluorine.

Some brines, volcanic gases, fumaroles, and hot springs with relatively high fluorine contents may suggest fluorine-rich provinces in which deposits of fluorspar, phosphate rock, or other fluorine materials should be sought. Deep sea sediments, which have more fluorine than most other marine sediments except phosphate rock, contain about 0.07 percent fluorine; these types of sediments and sea water itself, which has about 0.0001 percent fluorine, may be sources of fluorine in the distant future.

Numerous high-grade but small deposits of fluorspar, such as those of the Western United States, might be utilized. This use would require better techniques of locating and evaluating small pods of fluorspar and the use of portable extraction and processing equipment. Even though this type of mining may not be feasible now in the Western United States, because of high labor costs and land problems, it might be elsewhere in the world.

Very large low-grade multicommodity ores offer potential fluorine resources. These include deposits in which fluorine, mainly in the form of fluorite, is associated with metallic minerals (see discussions of geochemistry and exploitation) and those in which it is associated with or contained in other minerals of commercial interest, such as barite, bastnaesite, apatite, zeolites, and feldspars. It may be possible in the future to process such multicommodity ores, in which no single commodity is of high enough grade to be commercial.

PROSPECTING TECHNIQUES

Fluorspar deposits commonly have been found by identification of fluorite in outcrops and surficial materials. The durability of fluorite during weathering and the high fluorine content of the mineral suggest that some geochemical methods might be useful in prospecting for fluorspar. Nevertheless, geochemistry has not been widely used, in part because of the lack of rapid analytical procedures for determining, with the necessary reliability and low cost, the fluorine contents of samples.

A fluorine halo could be meaningless in fluorine exploration, inasmuch as fluorine is widely dispersed in many mineralized and altered areas other than those containing fluorine-rich deposits. Pathfinder elements can be used as a guide to some fluorine mineralization. To use this guide, however, requires considerable geologic knowledge of the area being surveyed. This approach avoids the problem of low-level fluorine analysis but will be successful only where the pathfinder element is consistently

associated with fluorine deposits. Friedrich and Plüger (1971) found that lead, zinc, and mercury contents of soils were useful guides in exploring for fluorite in Spain and that mercury was useful in the Wölsendorf district, Germany. If fluorite contains uranium minerals, as in the Thomas Range, Utah, and Jamestown, Colo., scintillation counters or Geiger counters might be helpful in prospecting for fluorspar.

Recent work in western North America has shown that fluorite deposits can effectively be sought by geochemical and heavy-mineral techniques. Fluorite persists for long distances during transport in the sediment of streams and can be concentrated therefrom with the gold pan. A systematic heavy-mineral survey near Winston, N. Mex., during 1970, by H. V. Alminas and K. C. Watts (oral commun., 1971), showed that fluorite is plentiful in sediment near two major subparallel north-trending faults, near the intersection of which an independent operator recently found a large fluorspar deposit.

Geochemical exploration investigations in the Browns Canyon district, Colorado, by Van Alstine (1965) showed that fluorine is found in abnormal concentrations in residual soil directly above and downslope from the principal vein and in alluvium downstream from the vein. The abundance of fluorine in those places may be due in part to the semiarid climate of the area. Van Alstine also pointed out that abundant biotite and hornblende increase fluorine values over that attributed to fluorite because of the fluorine content of the dark minerals. This problem is avoided by determining content of fluorite instead of fluorine.

Neither heavy-mineral nor geochemical prospecting methods for fluorite and fluorine have been well developed for fluorspar districts in humid regions. Geochemical studies of stream sediment and soils were found to be useful in prospecting for fluorine in the Hwanggangri region, Korea (Sang Kyu Yun and others, 1970).

Geophysical techniques have been utilized to some degree in evaluating mineralized areas that have fluorine potential. Electrical methods have been successful in outlining faults, some of which contain fluorspar (Hubbert, 1944), and alteration zones associated with fluorspar veins (Johnson, 1971). The refraction seismic method has been used as an indirect means of exploring for fluorspar in southern Illinois (Johnson, 1957). In general, it seems impracticable or impossible to detect minable bodies directly by methods of geophysical prospecting. The value of geophysical techniques is in finding locally mineralized faults, dikes, and altered zones, which then require geologic evaluation to determine fluorine potential.

PROBLEMS FOR RESEARCH

The distribution of fluorine in nature is only partly understood, and more research is needed on the geology and geochemical cycle of fluorine, especially on the partitioning of fluorine in geologic processes. Our present knowledge is not advanced enough even to adequately estimate crustal abundance, much less to accurately estimate resources. The fluorine content of igneous rocks serves as an excellent guide to potential fluorine deposits in the vicinity of such rocks; and yet, fluorine is commonly not determined in igneous rock analyses. Fluorine determinations should be made routinely in all chemical analyses of igneous rocks.

New techniques are needed to explore for and to evaluate fluorine deposits. Geochemical investigations of the fluorine content of rocks, soils, plants, and waters hold some promise as an exploration technique. However, for geochemical exploration to be useful, a quick, reliable, and inexpensive method of testing for fluorine needs to be developed.

Utilization of potential low-grade multicommodity ores as fluorine resources will require refinement and improvement of mining and processing techniques. Many of these low-grade deposits are very fine grained, and the fluorine minerals are intimately intergrown with other minerals, such as chalcedonic quartz, so that separation of the fluorine minerals is difficult.

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GALLIUM, GERMANIUM, AND INDIUM

By Robert A. Weeks

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ABSTRACT OF CONCLUSIONS

Known exploited sources of gallium, germanium, and indium are largely the ores of zinc and aluminum, from which they are recovered as minor byproducts. Potential additional sources are copper ores, tin ores, and combustion products of coal. The high cost of recovery and refining of gallium, germanium, and indium limits their use to relatively small quantities, mainly in transistors, diodes, and other electronic devices.

The geologic potential for finding deposits that could be exploited solely for their gallium, germanium, or indium content is very small. The potential for discovery of ores of other metals from which gallium, germanium, or indium could be recovered is significant. The potential for recovery of gallium and germanium from coal ash, flue dust, and stack gases in industrial plants consuming large quantities of coal is large.

INTRODUCTION

Gallium, germanium, and indium are three relatively rare metallic elements that occur in accessory or trace amounts in many rocks and minerals, including some in ores of other metals. Commercial recovery of these minor metals is, at present, entirely as a byproduct in the processing of major metallic ores, primarily zinc and aluminum, and to a lesser extent copper and lead.

There are no known deposits in which these metals are sufficiently concentrated that they are apt to be the principal product sought. None of them occur as native elements, and they are essential components in only a few very rare minerals. Their total value is small or even negligible in relation to the value of the principal metals with which they are associated. They are deleterious impurities and must be removed in refining the major metal. The complex technology for their recovery is economically feasible only if, at some stage in the processing of the major metal, the minor metal or metals become concentrated in a separable phase. The costs of their separation and purification are significant, and so recovery is limited to the amount of each that can be marketed. A further problem associated with such potential byproduct materials concerns the lack of data about the variability of specific individual ore sources, inasmuch as the processing plants do not normally maintain records for such minor constitu-

ents. The varied concentration of these byproduct materials in their primary ores is significant, although it is secondary in importance to the technology employed in processing the primary materials, inasmuch as the technology is what determines whether the initial gallium, germanium, and indium contents are concentrated or dissipated.

The principal physical and chemical properties of the three elements are listed in table 45. Gallium is notable for its low melting point and long liquid range and its expansion upon solidifying. Germanium also expands upon solidifying but is more notable for its high electrical resistivity in ultrapure form. Indium also melts at a low temperature but is notable for its softness and malleability.

TABLE 45.—*Selected properties of gallium, germanium, and indium*

Element	Gallium	Germanium	Indium
Atomic number	31	32	49
Atomic weight	69.72	72.60	114.6
Stable isotopes and, their abundance (percent).	69 (60.1) 71 (39.9)	70 (20.9) 72 (27.6) 73 (7.7) 74 (36.4) 76 (7 4)	113 (4.2) 115 (95.8)
Melting point (°C)	29.78	937	156.2
Boiling point (°C)	2,403	2,840	2,323
Density (g cm^{-3})	5.904 (solid) at 29.6°C. 6.095 (liquid) at 29.8°C. 5.446 at 1,000°C.	5.323 (solid) at 25°C. 5.589 (liquid)	7.31 at 20°C.
Expansion on solidifying (percent).	3.2	6	----------
Specific resistance (ohm-cm).	$0.38 \cdot 10^{-4}$ at 0°C	60 at 27°C $60 \cdot 10^{-6}$ at 937°C	$9 \cdot 10^{-6}$ at 20°C. $29 \cdot 10^{-6}$ at 156.4°C.
Color	Bluish white	Silvery white	Lustrous bluish white.
Hardness	Soft, ductile	Brittle, non-ductile.	Malleable, ductile.
Valence (most common shown in italic).	*4*, *3*, 2	*4*, 2	*3*, 2, 1

PRINCIPAL USES

The principal uses for gallium, germanium, and indium are as ingredients in transistors, diodes, and rectifiers, which are basic electronic components used in a wide variety of communications and control systems. The importance of these tiny devices in modern technology is difficult to overestimate—they perform the functions that formerly required vacuum tubes, but they do so with greater reliability, very small power consumption, negligible heat loss, extended durability, ruggedness, and compactness. Without these so-called solid state devices, the present generation of large computers would not have been feasible, because of the space, power requirements, and heat generated by an equivalent number of vacuum tubes. The amount of gallium, germanium, or indium used in each individual transistor or diode is quite small, but the very large number of such devices now being manufactured provides a significant market for these little-known materials.

Gallium, in addition to being used in these semiconductor devices, is used to modify other semiconductor materials, to form leads for transistor connections, and to provide a device that emits visible light as an indicator in various instruments. As an alloying ingredient, gallium forms a number of low-melting alloys of potential use. It also has potential application as a catalyst and in fluorescent materials.

Germanium is used dominantly in single-crystal high-purity form in the manufacture of transistors, diodes, and rectifiers. A typical transistor contains a wafer of germanium alloy 4 square millimeters in area and about 0.2 millimeters thick, whereas a diode is only about one-fourth as large, and rectifier crystals may be much larger. The weight of a transistor wafer is a few thousandths of a gram. In addition to major applications in communications and computers, germanium semiconductor devices have considerable use in nuclear radiation detection instruments. Germanium also is used in infrared equipment and in special optical glass. As an alloying ingredient, it increases hardness and improves rolling properties in alloys with copper, aluminum, and magnesium. It is used in gold solders and in jewelry manufacture. It is a constituent in several phosphors and has been used as a catalyst in polyester textile manufacturing.

Indium is used as a desired impurity in germanium and silicon transistors, as a solder for transistor leads, and in the fabrication of transistors, thermistors, and optical devices. It has been used in low-melting alloys and as a bearing alloy. It is used as a gasket material in aerospace hardware, as a sealant for glass-to-metal and glass-to-glass joints, in dental alloys, and in jewelry and silverware alloys to keep metals bright. Proposed uses include colorants for glass and as catalysts in petroleum refining.

ALTERNATE MATERIALS

Silicon in high-purity form is an alternate and less expensive material that competes extensively with germanium in the fabrication of transistors and diodes, and selenium and tellurium are used in rectifiers. Gallium, germanium, and indium can be used to some extent in substitution each for the other material. The specific characteristics of each, however, are unique in some applications, and therefore, complete substitution is not likely.

PROBLEMS IN DEVELOPMENT OF COMMERCIAL USES

The dispersed nature of the occurrences of gallium, germanium, and indium delayed the identification of these elements in to the latter part of the 19th century. The complex technology needed to recover each of them from dispersed sources has kept their prices at reasonably high levels. Their presence in ores of other metals is generally in such small quantities that they are not routinely analyzed for in commercial ore assays, nor has there been any reward to the producer for the gallium, germanium, or indium content of his ores.

Conventional treatment of these ores tends to eliminate the small content of the three metals as an inconspicuous part of the waste products. No major toxic effects have been reported from any of the three elements, so no special handling has been required to remove them from waste products. Each of these factors contributes to the overall situation that at present exists, in which the lack of a major supply precludes uses that would require significant tonnages of any of these metals, and conversely, the lack of a demand for significant tonnages precludes an intensive search for major additional sources of these metals.

The present industry recovers and refines only enough of each metal to satisfy existing markets, largely because the cost of refining is high and substantially equal to the market price. The recovery and refining processes are typically conducted as batch processes and for the most part have not operated on a full-time basis. In short, the recovery and refining of gallium, germanium, and indium have not been a major profit or operating factor in any operations to date.

Published data on production of the three materials have been limited by the relatively small number of producers. Table 46 presents estimated data, based on published sources, to provide some idea of the present extent of production.

RESOURCE AVAILABILITY

Gallium, germanium, and indium are so dispersed in nature that no deposits are known that could be exploited solely for their recovery. The commercial sources for these elements in the United States at present are as byproducts from the processing of zinc ores and, additionally for gallium, processing of aluminum ores. In the United Kingdom, germanium and gallium are recovered by processing fly-ash

TABLE 46.—*Estimated production, price, and apparent demand for gallium, germanium, and indium*

Year	Production (kg)						Price per gram			Apparent U.S. demand (kg)		
	Gallium		Germanium		Indium							
	U.S.	World [1]	U.S.	World	U.S.	World	Ga	Ge	In	Ga	Ge	In
1926	-----	-----	----	----	8	------	----	----	----	----	----	----
1930's	-----	----	----	----	----	+150/yr	$50.00	----	----	----	----	----
1941	-----	----	----	----	220	------	----	----	----	----	----	----
42	-----	----	<5	----	550	------	----	$5.00	$1.00	----	----	----
43	<10	----	<50	----	1,850	------	----	----	.50	----	----	----
44	<10	----	<50	----	2,565	------	----	----	.35	----	----	----
45	<10	----	<50	----	1,785	------	----	----	.25	----	----	----
46	<10	----	50–500	----	300	------	----	----	.072	----	----	----
47	<10	----	----	----	435	------	----	----	.072	----	----	----
48	90	----	----	500	380	------	4.50	----	.072	----	----	----
49	0	----	----	----	1,705	------	----	----	.072	----	----	----
1950	-----	----	----	----	3,910	------	4.50	----	.072	----	----	----
51	90	----	----	----	4,765	------	----	----	.072	----	----	----
52	0	----	----	----	----	------	3.50	.77	.072	----	----	----
53	-----	----	----	----	10,000	------	3.25	----	.072	----	----	----
54	-----	----	----	----	----	------	3.25	----	.072	----	----	----
55	-----	----	----	----	----	------	3.25	----	.072	----	----	----
56	-----	----	----	32,000	>3,035	------	3.25	----	.072	----	----	----
57	-----	----	----	----	------	------	3.25	----	.072	----	----	20,000
58	-----	----	----	----	[2]7,150	------	----	----	.072	----	----	----
59	90	----	----	[3]50,000–75,000		------	----	.32	.072	----	----	----
1960	-----	----	24,500			------	----	.295	.072	----	----	----
61	-----	----	18,150			------	----	.295	.072	----	----	----
62	-----	----	16,780			------	----	.295	.072	----	----	----
63	-----	----	9,070	----		------	.95–1.40	.25	.072	----	----	----
64	-----	----	9,070	68,945		------	----	.25	.074	----	----	----
65	-----	----	13,610	----		------	----	.252	.088	----	----	----
66	-----	----	13,610	----		------	----	.17	.088	----	----	----
67	-----	----	13,610	----		------	----	.17	.088	----	----	----
68	100–300	800–1,000	9,525	54,750	----	62,200	.60–1.75	.17	.08	200–400	47,200	17,100
69	-----	----	13,610	85,275	----	------	----	.185	.08	----	----	----
1970	-----	----	12,700	84,370	----	------	----	.271	.08	----	----	----
71	-----	----	12,250	88,000	----	------	.75	293	.08	----	----	----

[1] Total world production to 1965 about 5 tons.
[2] 10-year annual average, 1958–67.
[3] 4-year annual average, 1959–62.

from the combustion of coal. Additional potential sources of recovery exist in the processing of copper and lead ores and possibly in the processing of ores of other metals, including tin, tungsten, molybdenum, and arsenic.

The major resource problem therefore involves not so much the geologic occurrences of the three metals as the fate of the three metals during the processing of the ores for their major components.

From the scattered data on occurrence, apparently relatively little of the gallium, germanium, and indium potentially recoverable is now being obtained. Estimates of the germanium content of zinc ores, for example, suggest that potential resources are adequate to support a several-fold increase in annual production and the additional potential resources in coal would permit further expansion of production. Potential for recovery of additional gallium is also quite large, and the potential for indium is appreciable.

EXPLOITATION

Gallium, germanium, and indium have had similar histories. About half a century elapsed between the time they were first identified and the time that first commercial uses for them were developed. The growth in specific uses of the elements was undoubtedly retarded by the lack of natural sources of ores containing appreciable concentrations and by the relative difficulty of refining each of them from dispersed sources. Systematic study of their physical and chemical properties and investigation of their compounds and alloys are still progressing; thus, additional new uses will undoubtedly be found.

Recovery of indium on a semicommercial scale began in the 1920's for use as a precious-metal alloying agent to enhance brightness and retard tarnish. Additional uses developed in special bearing-metal alloys in the 1940's, but until the development of uses in semiconductor devices about 1952 the demand was not particularly steady. Similarly, germanium was not recovered in significant quantities until the early 1940's, when its use in electronic rectifiers led to initial commercial-scale production. With the development of transistors, beginning about 1948, germanium consumption increased greatly, and it continued to increase steadily through 1960, when there was a sharp decline in consumption because of competition from silicon and because of improvements in fabricating techniques. Gallium production began in 1943 with most of the few kilograms produced being used in research. With the development of semiconductor devices, production grew in the late 1940's and early 1950's to about 90 kg (kilograms) a year and has apparently stayed at about that level since then, with 1968 production estimated to be in the range of 100–300 kg. The present commercial production of each of the three elements is substantially smaller than might be achieved if there were larger markets. Recovery and refining are expensive; therefore, only the amounts that can be marketed are processed. The amounts recovered are obtained from several different intermediate products in the processing of ores of other metals. These starting materials in the recovery of the three metals generally represent the highest concentrations of gallium, germanium, or indium that can be obtained at some point in the production line where a separation can be made conveniently.

The principal products in which appreciable gallium, germanium, and indium are concentrated are recovered by roasting zinc sulfide ores to produce crude zinc oxide and by further roasting this with salt to separate the volatile chlorides of germanium, gallium, cadmium, and indium from the zinc. These chlorides are collected by electrostatic precipitation and purified by complex distillation, chemical treatment, and electrolytic separation.

In addition, the drosses, slags, and anode slimes in other smelting and refining processes can be used as starting materials, especially the materials that are associated with the recovery from zinc of other byproduct metals such as cadmium, lead, and tin. Gallium is also recovered from the leaching solutions used to make alumina from bauxite. At some stage in the caustic leaching cycle the solution builds up an equilibrium concentration of gallium (about 0.1 g per liter) which can be recovered by precipitation with carbon dioxide, filtration, and complex separation followed by electrolysis.

The complex chemical and physical processes used to separate and concentrate these metals have been developed primarily to operate on specific starting materials available to individual companies. For the most part, these starting materials are selected because they have the highest initial concentration of one or more potentially salable byproducts and because the particular starting materials can be conveniently acquired. Very few data are published on the trace-metals content of potential interest for other possible off-products at various stages of smelting and refining.

Judging from geochemical data on their germanium and indium contents, some copper ores, especially those containing enargite, bornite, tennantite, and tetrahedrite, would seem to be of particular interest as sources of these metals. The distribution of such trace metals in various stages of concentrating,

smelting, and refining have not been described in detail.

RELATION TO OTHER COPRODUCTS OR BYPRODUCTS

The interrelationship of these minor byproduct metals to other byproduct or coproduct metals is of particular interest. For example, the refining of cadmium from zinc plant residues offers an additional stage of processing in which germanium and indium may be volatilized and partly separated from other metals into an enriched product. Similarly, in the re-treatment of lead-bearing wastes in the refining of zinc, several metals, such as tin, bismuth, and indium, are concentrated in the dross skimmed from lead bullion. Recovery of these minor constituents and further separation account for most of the Canadian production of indium.

The economic viability of production of these minor metals from a particular source is not easily determinable. With limited markets, the search for additional sources has not been intensive. The recovery and separation methods have not yet been simplified to the extent that any one technique could be incorporated as a step in a continuous smelting or refining process.

ENVIRONMENTAL RELATIONSHIP

Both gallium and germanium, in limited amounts, are apparently taken up by plants. A germanium concentration of 10 ppm (parts per million) in the ash is reported to be the toxic limit for plants under experimental conditions. There are no reported occurrences of natural concentrations of germanium in soils above toxic limits. No toxicity in plants has been established for gallium or indium. Gallium is reported to be found in concentrations of 0.1–0.2 ppm in plant ash and has been detected in vegetable foodstuff and hens' eggs. No adverse environmental factors have been directly attributed to any of the three elements, although indium and its compounds have toxic properties to humans if ingested in large quantities, and massive ingestion of gallium compounds is also toxic.

GEOLOGIC ENVIRONMENT

GEOCHEMISTRY

All three elements are among the "dispersed" elements that tend not to form distinct minerals of their own, but to proxy for other major elements in most rocks and minerals.

Gallium is closely coordinated geochemically with aluminum, with which it is associated. Its ionic radius is 0.70 A in sixfold coordination (valence +3), permitting relatively easy substitution for aluminum (ionic radius 0.61 A). This association accounts for the thorough dispersal of gallium as a trace constituent in most igneous and sedimentary rocks, as shown in table 47. It also accounts for the relatively higher concentration of gallium in bauxite and other aluminous rocks. Gallium is also concentrated in sulfide minerals, especially the zinc sulfide minerals sphalerite (ZnS) and wurtzite ([Zn,Fe]S), in which concentrations of as much as 0.5 percent gallium have been reported. The concentration of gallium is reported to be higher in sulfide minerals formed at lower temperatures. Gallium is apparently absorbed by the organic matter in some plants and becomes concentrated in coal beds.

Germanium is closely coordinated with silicon and tin, and it can proxy for these elements in the crystal lattices of appropriate minerals. Germanium is distributed rather uniformly among the silicate minerals of most rocks. It is notably concentrated in topaz (as much as 700 ppm) and, to a lesser extent, in cassiterite, garnet, and micas from rocks rich in fluorine, such as some granite pegmatites

TABLE 47.—*Gallium, germanium, and indium contents of various materials*

[Crust and rocks, parts per million; waters, parts per billion]

Material	Gallium		Germanium		Indium	
	Usual range	Average	Usual range	Average	Usual range	Average
Continental crust	------	18	------	1.5	------	0.14
Igneous rocks:						
Ultramafic	1–5	2	0.7– 1.5	1	0.01–0.3	.07
Basaltic	9–20	15	.8– 3.2	1.3	.01– .3	.1
Intermediate	10–23	16	1.2– 6	1.6	.01– .9	.17
Silicic	14–30	19	.5– 4.7	1.6	.02– .5	.16
Alkalic	18–70	40	.9– 3.5	1.4	.01– .3	.07
Sedimentary rocks:						
Limestones	------	4	0– .8	.4	------	.01
Sandstones	3–20	8	0– 3.5	.8(?)	.03– .2	.06
Shales and clays	7–50	20	0– 3.9	2.2	.01– .7	.1
Bauxites	20–100	50	1.0– 3.6	2	.03– .2	.08
Coal	------	7	1 –150	5.5	------	--
Waters:						
Ground water	------	--	0– 24	.3(?)	------	--
Hot springs	------	--	.4– 44	10	------	--
Rivers	------	--	.03– .11	.05	------	--
Sea water	------	--	------	.06	------	--

and greisens. Germanium is appreciably concentrated in sulfide minerals, particularly sphalerite and wurtzite, which commonly contain 0.01–0.05 percent germanium and have been reported to contain as much as 0.5 percent germanium. Enargite (Cu_3AsS_4) commonly contains 0.01–0.1 percent germanium. Germanium is absorbed by the organic matter in plants and becomes concentrated in coal beds, especially in the uppermost and lowermost layers in a coal sequence. In weathering, germanium apparently enters the clay minerals and is slightly concentrated in shales.

Indium is not closely coordinated with any major element, and its distribution in nature is less well known. It has some association with tin, for which it apparently can proxy. It is a rare element, and notable concentrations are mainly limited to occurrences in sulfide minerals, especially sphalerite, which commonly contains 10–20 ppm and has been reported to contain as much as 1 percent indium in some specimens. Some copper-bearing minerals, particularly chalcopyrite and tetrahedrite, also have indium contents ranging from a few parts per million to 1,500 ppm.

ABUNDANCE

As shown in table 47, the estimated abundance of these three elements in rocks of the continental crust ranges from 18 ppm for gallium to 0.14 ppm for indium. Gallium is thus slightly less abundant than cobalt and considerably more abundant than various much better known metals such as tin, molybdenum, cadmium, and silver. Germanium, with an average abundance of 1.5 ppm, is as abundant as molybdenum and tin. Indium is slightly more abundant than silver. The fact that none of the three elements forms its own minerals, except in a few rare deposits, is largely a function of the chemical nature of the elements that permits them to substitute in trace amounts for other elements in a variety of common minerals.

Gallium in igneous rocks tends to occur in larger amounts in the more aluminous rocks, and within individual intrusions it is more concentrated in the later formed aluminous minerals. Highest concentrations are found in pegmatites, where gallium is most abundant in muscovite. Gallium tends to follow aluminum in the processes of weathering, although it may be slightly more mobile in normal soil-profile development. In the development of bauxite, however, the relative concentration of gallium increases with respect to aluminum. In sedimentary rocks only shales and clays tend to accumulate gallium. In metamorphic rocks there does appear to be a significant migration of gallium, although data are sparse. Gallium does not enter the biologic cycle to a significant extent, but it is taken up by some plants, where it is a minor component, presumably in an organic complex.

Germanium in igneous rocks is slightly more abundant in the silicic and intermediate rocks and is especially more abundant in the rocks developed in the late pegmatitic and pneumatolytic stages. In such rocks fluorine apparently provides a mechanism to transport and concentrate germanium into such minerals as topaz and cassiterite. In the weathering cycle, germanium is not notably concentrated in most processes but may be partly removed by surface waters. The bulk of the germanium content remains and is most likely in the clay minerals. The germanium content in living plants never exceeds 10 ppm in their ash, which is reported to be the toxic level in plants. The germanium content of coals ranges from a few parts per million to several hundred parts per million and is irregularly distributed laterally within individual coal beds and vertically within coal seams. Highest germanium contents are typically found in either the uppermost or lowermost layers. The germanium content is predominantly bound to the organic matter, coals with lowest ash content having the highest germanium content. Fly ash from coal combustion may contain as much as several percent germanium.

Very sparse data are available to indicate the distribution of indium. In igneous rocks it is slightly more abundant in intermediate and silicic rocks than in basaltic or alkalic rocks. It is notably concentrated only in pneumatolytic and hydrothermal stages. In sedimentary rocks it may be slightly concentrated in clays and shales. Data are insufficient to categorize its occurrence in metamorphic rocks, although slight enhancement of the indium content is suggested. Indium is not reported to be concentrated in plant ash or in coal.

ORE MINERALS

Gallium, germanium, and indium are concentrated in sulfide minerals, especially the zinc sulfide sphalerite. Table 48 lists the principal ore minerals that have been reported to contain appreciable amounts of any of the three elements, and where data exist, it gives some idea of both the range and the typical contents of these elements. The table also lists the rare minerals containing any of the three elements as essential components.

Of these rare minerals, most have been found mainly in studies of a single deposit, that at Tsumeb in South West Africa.

TABLE 48.—*Gallium, germanium, and indium contents of selected ore minerals and of reported gallium, germanium, and indium minerals*

Mineral name and composition	Gallium		Germanium		Indium	
Ore minerals (ppm)						
	Range	*Median*	*Range*	*Median*	*Range*	*Median*
Sphalerite, ZnS	1–10,000	40–50	5 –1,850	100–500	0.5–10,000	40
Galena, PbS	0– 500	----	0 – 10	------	0.5– 100	----
Chalcopyrite, $CuFeS_2$	0– 100	----	0.5– 900	10– 40	0 – 1,500	20
Enargite, Cu_3AsS_4	------	----	10 –5,000	10– 80	0 – 100	----
Bornite, Cu_5FeS_4	------	----	0 –1,000	------	1 – 1,000	----
Tennantite, $Cu_{12}As_4S_{13}$	------	----	0 –5,000	------	--------	----
Tetrahedrite, $Cu_{12}Sb_4S_{13}$	------	----	0 – 500	------	0.1– 160	----
Covellite, CuS	------	----	0 – 40	------	0 – 500	----
Chalcocite, Cu_2S	------	----	0 – 30	------	0 – 100	----
Pyrite, FeS_2	0– 100	----	0 – 100	------	0 – 50	----
Molybdenite, MoS_2	------	----	2 – 10	------	--------	----
Stannite, Cu_2FeSnS_4	------	----	6 – 20	------	5 – 1,500	50–500
Cassiterite, SnO_2	0– 50	----	5 – 200	10	0.5–13,500	22
Wolframite, $(Fe,Mn)WO_4$	------	----	--------	------	0 – 16	0– 10
Arsenopyrite, FeAsS	------	----	1 – 50	------	0.3– 20	3
Gallium minerals (percent)						
Gallite, $CuGaS_2$	35		--------		--------	
Sohngeite, $Ga(OH)_3$	49.6		--------		--------	
Germanium minerals (percent)						
Argyrodite, Ag_8GeS_6	------		7		--------	
Germanite, $Cu_3(Ge,Fe)S_4$	1.85		6.2–11.4		0.15	
Renierite, $(Cu,Fe,Ge,Zn)S$	0.55		5.9– 9.6		--------	
Briarite, $Cu_2(Fe,Zn)GeS_4$	0–2.2		13.7–16.9		--------	
Stottite, $FeGe(OH)_6$	------		29		--------	
Fleischerite, $PbGe(SO_4)_2(OH)_6 \cdot 3H_2O$	0.7		6.7		--------	
Itoite, $Pb_3Ge(SO_4)_2O_2(OH)_2$	------		Not available		--------	
Schaurteite, $CaGe(SO_4)_2(OH)_6 \cdot 3H_2O$	------		14.8		--------	
Indium minerals (percent)						
Indite, $FeIn_2S_4$	------		--------		59.3	
Requesite, $CuInS_2$	------		--------		46.3–47.8	
Sakuralite, $(Cu,Zn,Fe)_3(In,Sn)S_4$	------		--------		17 –23	
Dzhalindite, $In(OH)_3$	------		--------		Not available	

As shown in table 48, sphalerite is the mineral in which all three elements tend to be most concentrated. The exact nature of their incorporation into the crystal lattice of sphalerite is not fully known, but there do not appear to be distinct solid phases of the sulfides of any of the three elements, and each element is apparently able to proxy for zinc in the limited amounts found. There is some evidence that germanium and gallium contents are highest in the low-temperature varieties of sphalerite and that indium content is highest in medium-temperature varieties of sphalerite. Thus, zinc ores from low-temperature deposits such as the upper Mississippi Valley and Tri-State districts tend to have among the highest reported gallium and germanium contents but not the highest indium content.

Other sulfide minerals that have major concentrations of germanium are chalcopyrite, bornite, enargite, and tennantite. Major concentrations of indium have been reported in cassiterite, especially in the "wood tin" variety, in which the concentration may typically exceed 0.5 percent indium. Stannite, another tin-bearing mineral, also has been reported to contain significant indium concentrations.

TYPES OF ORES

The present major sources of gallium, germanium, and indium are zinc and bauxite ores, which are more fully described in the chapters on zinc and aluminum resources.

SULFIDE ORES

Far too few data are available to indicate the variation in distribution of any of the three elements in specific zinc deposits or within districts or broader regions. The sparse data suggest that there may be geologic provinces in which one or all of these elements are relatively more abundant in the intermediate to silicic igneous rocks, and that late-stage pneumatolytic and hydrothermal deposits associated with these rocks might be correspondingly enriched. The relatively higher gallium and germanium content noted in sphalerites formed at lower temperatures indicates a beginning of attempts to unravel the specific distribution patterns for these elements.

The geologic environment most favorable for large zinc sulfide ore deposits is in sedimentary sequences which include carbonate rock strata that have been permeated by mineralizing solutions. The source of

mineralizing solutions for some deposits is clearly associated with nearby igneous intrusions. For a significant number of major districts, however, the source of mineralizing solutions is equivocal. The Mississippi Valley and the Tri-State districts, in which gallium and germanium are relatively highly concentrated, are included in the group of deposits which have no closely associated intrusive bodies. The unique Tsumeb deposit in South West Africa is a pipelike body cutting a dolomitic sequence; it consists of a core of aplitic or pseudoaplitic rock surrounded by a shell of replaced carbonate rock containing lead, copper, and zinc sulfides with sparse amounts of germanite and renierite intergrown with galena and tennantite.

From the sparse data available, the occurrence of gallium, germanium, and indium in sulfide deposits is governed by their ability to coprecipitate with zinc in environments favorable to metal sulfide deposition. Apparently the concentration of gallium, germanium, and indium in mineralizing solutions is small, and in only a few deposits, notably at Tsumeb, has the concentration exceeded the maximum level at which they are able to enter the crystal lattice of sphalerite and other sulfide minerals.

In addition to occurring in zinc deposits, germanium is notably concentrated in some sulfide ores of copper, especially in deposits containing enargite, bornite, or tennantite, such as those at Butte, Montana; Chuquicamata, Chile; Cerro de Pasco, Morococha, Quiruvilca, and Casapalca, Peru; and Bor, Yugoslavia. The germanium content of enargite typically may be higher than it is in many zinc deposits. Complex sulfide copper ores containing tin, antimony, and arsenic, as well as many tin ores such as those in Bolivia, contain significant indium and some germanium and gallium. Lead ores and complex lead-zinc-copper ores also may be potential sources. These ores of metals other than zinc in general have not provided major sources for recovery of germanium or gallium but have been the source of some indium production.

BAUXITE

Gallium is also concentrated in bauxite, which forms through intensive weathering of different kinds of aluminous rocks. For the Arkansas bauxite deposits, a slight increase in the gallium-aluminum ratio during bauxitization has been shown in comparing a series of analyses of fresh nepheline syenite, partly bauxitized rock, and high-grade pisolitic bauxite. This increase has been attributed to the lower solubility of gallium hydroxide compared with aluminum under reducing conditions. Typical gallium contents of bauxites range from 20 to 100 ppm, the higher values being found in bauxites developed from granitic and alkalic rocks. There are no systematic studies of the lateral variation of gallium content in bauxite deposits, but the few data available suggest that lateral variation could be very slight.

In the less intensely weathered high-alumina clays that have been considered as potential resources of aluminum, the gallium content is generally in the range of 30–60 ppm.

COAL DEPOSITS

Germanium and gallium both are found in very small concentrations in living plants, but no specific function has been attributed to their presence. Plant residues typically show some enrichment in both elements. The germanium and gallium content of many coal beds is notably high and is greatest in the uppermost or lowermost parts of individual coal seams. The germanium content of coal typically ranges from a few to a few hundred parts per million, and it may increase to a few tenths of a percent in the ashes formed by combustion of the coal. Gallium content in coals is not as variable, but it also increases from a few tens of parts per million in most coals to a tenth of a percent or more in selected combustion products.

The variability of germanium content in coal seams is largely attributed to the reaction of complex humic acid hydroxyl groups with germanium-bearing water in such a way that any germanium released by plant decay or entering from outside the coal-forming environment is promptly incorporated or adsorbed in the organic complex. The gallium content presumably is similarly enhanced during coalification. The higher content of both metals in the upper and lower parts of coal seams is attributed to the greater volume of water passing through or adjacent to these parts of the coal beds during their formation because of the low permeability of the enclosing clayey strata.

RESOURCES

The known reserves of gallium, germanium, and indium are closely associated with currently exploited zinc and aluminum ores and with coal deposits that are supplying fuel to a few power plants in Great Britain. Additional potential resources are known, but much of the ore from which these metals might be recovered currently is processed without separation of these minor constituents. The extent of recovery in the future depends both on better recovery technology and on increased demand for

the three metals. Ores of metals other than zinc and aluminum, especially some copper and tin ores, appear to have interesting concentrations of one or all of these metals and might become important sources. Recovery of germanium and some gallium from industrial coal ash, flue dusts, and stack gas is feasible and would increase the recoverable recoverable resources of these two metals significantly.

RESERVES

The U.S. Bureau of Mines has estimated the recoverable supplies to the year 2000 for these three metals, on the basis of 1968 technology and prices, and projected demands for the major metals with which they are associated, as follows:

	United States (kg)	*World (kg)*
Gallium:		
Total potential in bauxite and zinc ores likely to be produced to year 2000	2,700,000	Not available
Recoverable	27,000	Not available
Germanium: recoverable from lead-zinc ores	375,000	1,360,000
Additional potential, assuming recovery from coal consumed in industrial plants	545,000	4,500,000
Indium: recoverable from lead-zinc ores (assumes some increase in zinc prices)	1,460,000	3,360,000

These estimates are necessarily conservative in that present low recovery ratios have been used and no new technology is assumed. Some uncertainties have been introduced in these figures by the closing of several older U.S. zinc smelters in the period 1970–72, which resulted in the reduction of domestic zinc smelting capacity by as much as a third. The figures provide at least the order of magnitude for amounts of the three metals that may be obtained in the next few decades at expected prices and using present technology. The figures suggest that any potential new uses requiring large amounts might require an associated increase in production through better technology or exploitation of additional sources.

POTENTIAL RESOURCES

On the basis of a simplistic assumption that all sphalerites contain gallium, germanium, and indium and that the estimated zinc reserves are all present as sphalerite, calculation of the amount of these three metals using median figures given in table 48 suggests that about 2 million kg of gallium, 13.5 million kg of germanium, and 1.8 million kg of indium might be contained in the recoverable portion of identified U.S. zinc resources described in the zinc chapter of this volume. If presumed identified resources are also included, these figures would be approximately three times larger. World identified recoverable zinc resources would contain on the order of 10 million kg of gallium, 70 million kg of germanium and 9 million kg of indium.

About 2,400,000 kg of gallium may be present in identified domestic bauxite resources, and 12–18 million kg of gallium in potential domestic resources. World resources of gallium contained in bauxite are probably on the order of 50 times larger than the domestic resources just cited.

The amounts of gallium and germanium that might be contained in coal combustion products are less easily estimated, but the U.S. Bureau of Mines estimate suggests about 500,000 kg of germanium could be obtained from coal used in U.S. industrial plants, with a world figure at about 10 times that amount.

The potential for recovery from ores of other metals has not been enumerated. At least for germanium, the content in identified domestic copper ores containing significant enargite, tetrahedrite, and tennatite might exceed 160,000 kg. On a world basis, the gallium, germanium, and indium contents of copper and tin ores are too poorly known to estimate their additional potential.

PROSPECTING TECHNIQUES

Prospecting techniques for each of the major resources with which gallium, germanium, and indium are associated are described elsewhere in this volume and will not be repeated. Even if major new uses for one or all of these elements were to be developed that would require greatly expanded production and associated price increases, there is very little geologic probability of finding ores that will be exploited solely for their gallium, germanium, or indium contents.

Much information needs to be obtained and natural distribution patterns need to be defined before specific guides can be determined for each element. Their geochemistry is still imperfectly understood, especially the variability of each within specific deposits and the range of variability in different geologic settings. The accumulation and analysis of such data is the next logical step in establishing a better basis for identifying favorable deposits and estimating resource availability.

PROBLEMS AND NEEDS FOR ADDITIONAL RESEARCH

Resource studies of minor byproduct metals are limited by inadequate data. Although data have been published on germanium production in recent years, no production data are available for gallium and indium. Specific identity of original sources of byproduct materials is not maintained for these three metals.

The data on geologic distribution of these trace metals have not been systematically assembled; therefore, distributional patterns in individual deposits are not well known, and regional variations have not been established. To the extent that commercial recovery of these materials might be feasible from sources other than those currently being exploited, much research is needed to establish the natural distribution pattern.

The most promising areas of research would seem to be in studying the distribution of these trace metals in zinc and copper ore deposits and in making a systematic compilation of the metals' regional variations.

In the broader area of commercial recovery, there appears to be significant concentration of these metals that might be recovered in the processing of other ores, particularly copper ores. Search for concentration of these metals in various smelting and refining products of all metallic sulfide ores is needed.

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GEM STONES

By Robert E. Thaden

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ABSTRACT OF CONCLUSIONS

Gem stones are mineral substances, other than metals, that are attractive enough for use in personal adornment or as small household objects. More than 230 mineral species are, or have been, used as gem stones at one or another stage of man's cultural history. Gem stones ideally possess beauty, durability, and rarity, but the value of a stone may be enhanced considerably by masterful cutting. Diamond, sapphire, ruby, and emerald generally are considered precious stones; all other gem stones generally are considered semi-precious. Neither imitation nor synthetic gems have infringed seriously on the market for natural stones, nor are they likely to do so. Gem stones occur in most of the major geologic environments, but they do not form ore deposits in the normal sense. Since 1935, the mining of gem stones in the United States has been almost entirely a recreational activity of mineral collectors and hobbyists. The annual value of such gem production has risen from half a million dollars in 1952 to nearly $3 million in 1972. A little over $500 million a year is spent for importing gems, mostly cut and uncut diamonds, and about $200 million worth of cut diamonds and synthetic gems are exported annually.

INTRODUCTION

Gem stones are mineral substances, other than metals, that are attractive enough for use in personal adornment or as small household objects such as book ends, pin boxes, and statuettes. Gem stones are mostly, but not exclusively, of inorganic origin. Some vegetable substances, such as amber, and the cannel, anthracite, and jet varieties of coal are included, as well as some organically precipitated mineral materials, especially pearl and coral.

A large number of minerals have been used as gem stones at one or another stage of man's cultural history, mostly depending on availability or fashion. An inventory of more than 230 mineral species that now have or have had currency as gems—nearly one-tenth of all known minerals (Fleischer, 1971)—can easily be compiled from published lists of gems and gem localities (Ball, 1931; Jahns, 1960; Schlegel, 1957; French, 1968).

Ideally a gem stone should possess beauty, durability, and rarity. Beauty, of course, is in the eye of the beholder and varies with the individual and with the culture in which he lives. Beauty is based on an appreciation of certain attributes of the stone—its color, clarity, optical dispersion, index of refraction, and perfection of chatoyant zones, to name a few. Durability encompasses other physical properties including chiefly resistance to scratching, which is a measure of innate hardness; resistance to cleavage and fracture; and insolubility. Rarity appeals to human exclusiveness and perhaps for this reason usually is the principal control over the value assigned to stones. Rarity, however, can act in the opposite manner; Jahns (1960) has stated that some stones, even those having all the other desirable attributes, are so rare as to be undependable in supply, to be virtually unknown, and therefore to command no market. Examples given by Jahns include the beautiful oil-green and reddish-brown strongly dichroic andalusite, and transparent phenakite, euclase, and staurolite. Others also could be named—transparent cassiterite, brazilianite, and lapis lazuli. Some stones are a matter of national pride and are far more expensive in their country of origin than elsewhere. Alexandrite (chrysoberyl) from the U.S.S.R. is the prime example.

Another characteristic, independent of the physical properties important in determining the value of

the stone, is the "make," a measure of the degree to which the lapidary has enhanced the physical characteristics of a stone. Enhancement is accomplished by orienting, proportioning, accurately shaping or faceting, and polishing the gem to display most effectively its optical properties in an esthetically satisfying form.

Almost no gem stones meet the ideal definition that requires beauty, durability, and rarity; and some have no redeeming virtue but beauty. It is obvious, then, why those few stones—diamond, sapphire, ruby, and emerald—that have these three qualities to a high degree always have commanded a high price and always have been thought of as precious stones, in contrast to others considered to be only semiprecious. At certain times and places opal, chrysoberyl, and even pearl, turquoise, and amber also have been considered precious stones, largely on the basis of their rarity. Pearl and turquoise are now reasonably abundant and therefore reasonably inexpensive. On the other hand, vanishingly small supplies of stones of exceptional size and quality allow ruby and Uralian alexandrite to command prices far in excess of that asked for diamond of the same weight. Other stones increase in price faster than can be accounted for by inflation, increasing rarity, or national pride. Aquamarine and tanzanite (a variety of zoisite), for instance, have risen rapidly in price recently in some parts of the world, apparently very largely in response to changes in style of personal ornamentation—that is, in response to fad. The exhaustion of ancient mining areas, the discovery of new deposits, shifting tastes, development of synthetic stones, and changes in pattern of transportation and marketing have combined to break down these distinctions; so the tendency is for all gem materials now simply to be known as precious stones.

EXPLOITATION

A very large fraction of all the gem materials ever produced is still in existence because of the inherent durability of stone, however soft, and the care normally lavished on costly artifacts. With the constant discovery of new gem deposits, it might be expected that the supply eventually would satisfy the market. But the market constantly grows, along with world population and affluence, and the attendant social and political unrest puts an additional premium on gems, for they constitute an easily portable and concentrated form of wealth. The price of any gem material is not likely to drop except over the short term.

Neither imitation nor synthetic gem stones have infringed seriously on the market for natural stones, nor are they likely to do so in the future, in spite of the already wide variety and crystalline perfection of these materials and the nearly frantic research to produce others. Ruby, sapphire, spinel, rutile, emerald, garnets, lapis lazuli, greenockite, diamond, and a number of other gems have been synthesized. Some of these, in both colored and colorless forms, together with several natural gems and other synthetic materials such as strontium titanate and yttrium-aluminum garnet (YAG), are marketed as inexpensive substitutes for natural diamond. Colored glass and imitation pearls, of course, fill the need for costume jewelry. Like Rembrandt originals, however, natural gem stones will always be assured a market because of the exclusiveness of rarity and genuineness, regardless of the disparity in price between them and their substitutes.

Persistent commercial production of gem stones at a profit by a private corporation is a rarity anywhere in the world. The rich diamond pipes of Africa and the alluvial diamond deposits in Africa and in Brazil are significant exceptions. The profitability of government-owned mines, such as the emerald mines of Colombia and West Pakistan and the diamond deposits of Soviet Siberia, is not known. It is a fact, however, that the privately operated Chivor emerald mines in Colombia are now idle, perhaps in part because a reported large fraction of production was lost through pilferage and never reached the company's vaults. Commercial ventures to produce sapphire and ruby in Burma and in the Yogo Gulch area of Montana were short lived, as was the attempt to produce diamonds from the kimberlite pipes at Murphreesboro, Ark., and the same is true at many other places throughout the world. The small size and diffuse nature of most deposits of gem materials seem to make them amenable to exploitation only by the individual miner or small group, often a family, many of whom mine stones only intermittently and by relatively unsophisticated methods. Yet the bulk of all gem stones exclusive of diamond and emerald are produced in this manner, whether they come from the pegmatites of the Malagasy Republic, Brazil, Maine, or California, or from the alluvial deposits of Burma, Ceylon, or Idaho.

GEOLOGIC ENVIRONMENT

It is no tautology to say that gem stones are rare because they are not plentiful. They do not form "ore" deposits in the normal sense. The very precise environmental conditions required to produce gem stones, any gem stones, are unusual in the context of the large scale and constantly changing chemical-thermal-dynamic systems in which all minerals are formed. Gems, when present at all, generally are

scattered sparsely throughout a large body of rock, or have crystallized as small aggregates or fill veins and small cavities. Even placer concentrations tend to be small—a few stones in each of several bedrock cracks, potholes, or gravel lenses in a streambed. The average grade of the richest diamond pipes in Africa is about 1 part diamond in 40 million parts "ore," and because much diamond is not of gem quality, the average stone in a woman's engagement ring is the product of the removal and processing of 200–400 million times its volume of rock.

Gem stones occur in most of the major geologic environments. Each environment produces a characteristic suite of gem materials, although many gems occur in more than one environment.

The igneous rocks are the source of the greatest value of gems each year largely because the kimberlites in Africa (see chapter on "Abrasives") yield most of the world's diamonds. Other mafic igneous rocks yield ruby, sapphire, garnet, and peridot, and probably also, at least in some places, jadeite and nephrite. Granitic igneous rocks, particularly the coarsely crystalline pods and tabular bodies called pegmatites, and coarsely crystalline fillings of miarolitic cavities, probably contain a wider variety of gem stones than any other rock type. Quartz, tourmaline, topaz, apatite, spodumene, and beryl (including emerald), in all their varieties and colors, as well as zoisite, garnet, chrysoberyl, sphene, spinel, and zircon, are characteristic of pegmatites and igneous cavity fillings.

Metamorphic rocks are the source of ruby, saphphire, garnet, and emerald. The schists and gneisses also contain andalusite, actinolite, chrysoberyl, zoisite, topaz, jadeite, and nephrite, whereas the additional suite of gem stones characterizing the marbles and related calcareous metamorphic rocks includes rhodonite, lazurite, epidote, cordierite, apatite, axinite, and tourmaline. Contact-metamorphosed rocks are likely to be more productive of a variety of gem materials than those that have been regionally metamorphosed; the igneous rock bodies nearby supply fluid emanations containing the constituents needed to form some of the gem minerals.

Aqueous solutions, both the hot solutions derived from plutonic igneous bodies or from volcanic activity and the relatively cold solutions that percolate downward into the rocks from the surface of the earth, are the source of a rich variety of gem materials which precipitate in cracks, fissures, and voids or replace preexisting materials. Some gems precipitate only from waters that are at least reasonably hot; examples are euclase, citrine quartz, imperial topaz, emerald, and benitoite. Other gems can precipitate from aqueous solutions having a wide ranges of temperature—cacoxinite and amethyst, for example, as well as opal, pumpellyite, datolite, thomsonite and the other zeolites, hematite, tourmaline, some topaz, and certain garnets. Cold-water solutions descending through the rocks are the source of most agate, jasper, petrified wood and bone, and tigereye and other forms of cryptocrystalline quartz, and they also supply the oxygen needed to alter preexisting mineral materials to such gem materials as malachite and turquoise.

When a primary deposit of gem stones is weathered deeply, as is common in many parts of the world, the gems are left behind in a clayey matrix from which miners can easily wash them. Nearly all mining of gem-bearing rock is confined to the weathered zone because of the difficulty of freeing gems from fresh rock without shattering them.

A placer deposit is formed when wind or water removes clayey matrix from a weathered gem-bearing rock body leaving the gems concentrated. Placers generally are far richer than the original sources because of the concentration process and because the imperfect gem stones tend to be eliminated by breakage, leaving behind the gems of exceptional quality.

UNITED STATES OCCURRENCES

Nearly 100 different mineral species have been mined and marketed in the United States as gem stones, and every state has contributed to this market. Most deposits consist of "semiprecious" stones. Even quasi-gem materials such as banded rhyolite, porphyritic andesite, clusters of marcasite crystals, and fossil trilobites have commercial value in the fabrication of pins, broaches, tie slides, and similar items. The United States also has produced diamond from Arkansas and ruby and sapphire from Montana and the Appalachian States, especially North Carolina; North Carolina also continues to produce an occasional emerald. Maine was at one time known for its commercial production of colored tourmalines and beryl. Large quantities of pink tourmaline from the Pala district of California were sent to China in the early part of this century. Wyoming and California continue to produce large quantities of the jade minerals, but production from vast jade fields in the Kobuk River region of Alaska is just beginning. Benitoite is known to occur nowhere in the world except in California, and the rhodolite garnets of North Carolina and the pumpellyite amygdules from the western end of Lake Superior are, as far as is known, unique.

Large deposits of the more valuable gem materials that can be and have been mined for centuries such

as the abundant pegmatites of Brazil and the Malagasy Republic, or the extensive placer deposits of southern Asia, are not known in the United States. The few American deposits which produced ruby, sapphire, emerald, beryl, and tourmalines commercially ceased doing so years ago. Since about 1935 the production of gem stones in the United States has been restricted very largely to turquoise, jadeite, nephrite, opal, aventurine, and the cryptocrystalline silica minerals agate, petrified wood, chalcedony, chrysoprase, and jasper. In total value the silica minerals overwhelm all the others. Nearly all the gem stone production of the last 40 years has come from Texas and the States west of the Great Plains, but it is impractical to enumerate here all of the gem stone localities of even the Western States.

UNITED STATES PRODUCTION

The mining of gem stones in the United States since about 1935 has been almost entirely a recreational activity of mineral collectors and hobbyists. Estimates of the number of individuals in recent years whose entire income is derived from gem stones mined by themselves have ranged from only 8 to about 30. This is not to say that the proprietors of roadside rock shops buy all of their stock from others. Rock shops are abundant in areas rich in gem materials, and the operators tend to specialize in the local gem commodities, most of which they gather themselves. Owners of properties containing gem materials, rather than doing the mining themselves, sometimes charge hobbyists for the privilege of collecting gem stones. Diamond in Arkansas, opal in Idaho, and agate in Oregon and Washington are mined by hobbyist under this type of "fee digging" arrangement. it is not usually, however, the value of the stones produced and sold in an area or the generally small fees collected by property owners that are the most significant contributions to the local economy of areas productive of gem stones; rather, it is the cost-of-living expenses of the hobbyists while afield. Moreover, with the growing popularity of lapidary work and of "rock hounding" among all age groups in the United States, and with the steadily increasing number of older people, many of whom are retired and have time available to pursue the hobby, both gem production and the economy of gem-producing areas are likely to increase substantially in the future. It is not paradoxical, therefore, that the United States, which has no major gem stone deposits and no organized gem-producing industry, still has been able to increase the value of its gem production from half a million dollars in 1952 to nearly $3 million in 1972; the annual value of gem stones produced 20 years hence probably will be several times $3 million.

IMPORTS AND EXPORTS

The United States is a large importer of gems, mostly the "precious" stones diamond and emerald, of which the United States has only minuscule domestic production. Diamond once made up nearly 95 percent of all gem imports; and although it has now dropped to about 80 percent, current import of cut diamond is about $200 million annually, and import of uncut diamond is about $300 million. Cut emerald is imported at a rate of about $10 million annually, and in some recent years the import of synthetic stones has been nearly this much. Pearls and other gem materials, including imitation stones, constitute only a few percent of the value of all gems imported.

The value of gem stones exported from the United States is about $200 million per year. The reexport of diamond, cut in this country from imported uncut stones, accounts for much of this, but an increasing percentage is made up of synthetic stones. There is also a small but steadily increasing export of natural domestic gem materials to Germany, Taiwan, and elsewhere for fabrication. Principal among these materials are turquoise and the jade minerals, as well as quantities of massive actinolite, pink dolomite, banded rhyolite, and other ornamental stones.

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GEOTHERMAL RESOURCES

By L. J. P. Muffler

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ABSTRACT OF CONCLUSIONS

The geothermal resource base is defined as all the heat above 15°C in the earth's crust, but only a small part of this resource base can properly be considered as a resource. The magnitude of the geothermal resource depends on the evaluation of many physical, technological, economic, environmental, and governmental factors. The physical factors that control the distribution of heat at depth can be evaluated, at least rudely. More tenuous are the assumptions of technology, economics, and governmental policy. These assumptions are critical to geothermal resource estimation, and differences among them are in great part responsible for the vast range in magnitude among different geothermal resource estimates.

Utilization of a greater proportion of the geothermal resource base depends on achieving one or more of the following items:

1. Technological advances that would allow electrical generation from low-temperature reservoirs.
2. Breakthroughs in drilling technology that would permit low-cost drilling of holes to depths greater than 3 km.
3. Development of techniques of artificial stimulation that would increase the productivity of geothermal reservoirs.
4. Expansion of the use of low-grade geothermal resources for such purposes as space heating, product processing, agriculture, and desalination.

INTRODUCTION

Geothermal energy, in the broadest sense, is the natural heat of the earth. Temperatures in the earth rise with increasing depth. At the base of the continental crust (25–50 km), temperatures range from 200°C to 1,000°C (Lachenbruch, 1970); at the center of the earth (6,371 km), they range perhaps from 3,500°C to 4,500°C. Most of the earth's heat is far too deeply buried ever to be tapped by man. Although drilling has reached 7½ km and may some day reach 15–20 km, the depths from which heat might be extracted profitably are unlikely to be greater than 10 km. Even in this outer 10 km, most of the geothermal heat is far too diffuse ever to be recovered economically (White, 1965). Consequently, most of the heat within the earth, even at depths of less than 10 km, cannot be considered an energy resource.

Geothermal energy, however, does have potential economic significance where heat is concentrated into restricted volumes in a manner analogous to the concentration of valuable metals into ore deposits or of oil into commercial petroleum reservoirs. At present, economically significant concentrations of geothermal energy occur where elevated temperatures are found in permeable rocks at depths less than 3 km. The thermal energy is stored both in the solid rock and in water and steam that fill pores and fractures. This water and steam serve to transfer the heat from the rock to a well and thence

to the ground surface. Under present technology, rocks with too few pores, or with pores that are not connected, do not constitute an economic geothermal reservoir, however hot the rocks may be.

Water in a geothermal system also serves as the medium by which heat is transferred from a deep igneous source to a shallow geothermal reservoir at depths shallow enough to be tapped by drill holes. Geothermal reservoirs are located in the upflowing parts of major water convection systems. Cool rainwater percolates underground from areas that may consist of tens to thousands of square kilometers. At depths of 2–6 km, the water is heated by contact with hot rocks (in turn probably in contact with molten rock). The water expands upon heating and then moves buoyantly upward in a column of relatively restricted cross-sectional area (1–50 km^2). The driving force of these large circulation systems is gravity, effective because of the density difference between cold downward-moving recharge water and hot, upward-moving geothermal water.

EXPLOITATION

The primary use of geothermal resource to date is for the generation of electricity (fig. 27). Under existing technology, geothermal steam (after separation of any associated water) is expanded into a low-pressure (5–7 bar) turbine which drives a conventional electrical generator. Geothermal heat is also used directly (table 49) in the heating and air-conditioning of buildings, in the heating of hothouses and soil for agricultural purposes, and in product processing. In addition, warm waters from springs and wells are widely used for bathing, recreational, and therapeutic purposes, particularly in central Europe and in Japan (Komagata and others.

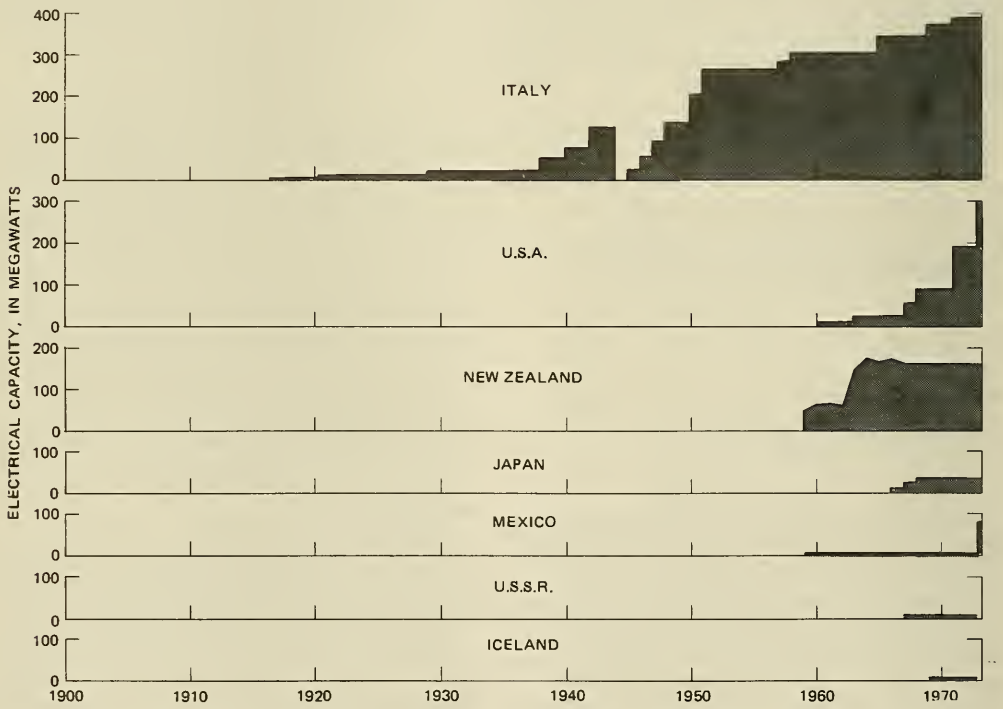

FIGURE 27.—Growth of geothermal generating capacity by countries 1900–72. Sources—Italy: [Italy] ENEL, [1970]. U.S.A.: Bruce (1971). New Zealand: McKenzie and Smith (1968); Smith (1970). Japan: Hayashida and Ezima (in press); Mori (in press). Mexico: Alonso-Espinosa and others (1968). U.S.S.R.: Tikhonov and Dvorov (1970); Facca (in press). Iceland: Ragnars and others (1970).

TABLE 49.—*Principal utilization (other than for electricity) of geothermal resources*

Use	Country	Localities	Quantity	Reference
Space heating	Iceland	Reykjavik	1.08×10^{15} cal yr^{-1} in 1969	Pálmason and Zoëga (1970).
		Hveragerdi, Selfoss, Saudárkrokur, Olafsfjördur, and Dalvik.	8.8×10^{13} cal yr^{-1} in 1969	Do.
	Hungary	Various localities	Peak load 3.9×10^{11} cal hr^{-1}; "Optimal useful production capacity"=1.1×10^{15} cal yr^{-1}.	Boldizár (1970).
	U.S.S.R	Caucausus Mountains, Kazakhstan, Kamchatka.	Uncertain but large	Makarenko and others (in press), Sukharev and others (in press), and Tikhonov and Dvorov (in press).
	New Zealand	Rotorua	~950 wells	Burrows (1970).
	United States	Klamath Falls, Oreg	$\sim3\times10^{13}$ cal yr^{-1}	Peterson and Groh (1967).
		Boise, Idaho	Capability of $1-2\times10^{6}$ gal yr^{-1} of 75°C. water.	Koenig (1970).
Air conditioning	New Zealand	Rotorua	5.8×10^{5} cal hr^{-1} heat input to LiBr absorption unit.	Reynolds(in press).
Agricultural heating	Iceland	Hveragerdi	$>9.6\times10^{4}$ m^2 of greenhouse in 1960; 6.3×10^{13} cal yr^{-1} in 1969.	Pálmason and Zoëga (1970).
	U.S.S.R	Various localities	2×10^{7} m^2 of greenhouse in 1969	Dragone and Rumi (in press).
	Hungary	----do	$\sim4\times10^{5}$ m^2 of greenhouse in 1969	Boldizár (1970).
	Japan	----do	$\sim2\times10^{4}$ m^2 of greenhouse	Komagata and others (1970).
	Italy	Castelnuovo	3×10^{3} m^2 of greenhouse	Dragone and Rumi (in press).
	United States	Lakeview, Oreg	2.3×10^{3} m^2 of greenhouse	Head (1970).
Product processing:				
Paper	New Zealand	Kawerau	$\sim9\times10^{14}$ cal yr^{-1}	Calculated from Smith (1970, table 10).
Diatomite	Iceland	Námafjall	$\sim2\times10^{14}$ cal yr^{-1}	Ragnars and others (1970, table 3).
Salt	Japan	Shikabe, Hokkaido	150 tons yr^{-1} of salt recovered from sea water.	Komagata and others (1970).
Byproducts:				
Dry ice	United States	Imperial Valley, Calif	$>1.84\times10^{7}$ m^3 of CO_2 between 1934 and 1943.	Muffler and White (1968).
Boron	Italy	Larderello	Large production from 1810 to 1966	----------
Calcium chloride	United States	Imperial Valley, Calif	Uncertain but small	----------

1970). Geothermal energy has potential use in refrigeration and freeze drying (Einarsson, 1970), and some geothermal fluids contain potentially valuable byproducts, such as potassium, lithium, calcium, and other metals (White, 1968).

Production of fresh water by self-desalination of geothermal fluids has been proposed for the Imperial Valley in Southern California (Rex, 1968, 1971b) and for the El Tatio geothermal field in northern Chile (Barnea, 1971). Evaluation of the geothermal desalination potential of the Imperial Valley is being carried out jointly by the U.S. Bureau of Reclamation and the Office of Saline Water (U.S. Bur. Reclamation, 1972). The quantities of geothermal water in storage in the Imperial Valley are large (Dutcher and others, 1972). If geothermal desalination proves to be technologically and economically feasible, the waters of the Imperial Valley may prove to be a significant augmentation to the fresh water supply of the southwest United States.

ENVIRONMENTAL CONSIDERATIONS

Considerable attention has been drawn to geothermal resources as an electrical generating mode that can have a relatively small effect on the environment. Geothermal energy does not produce atmospheric particulate pollutants as do fossil-fuel plants, and it has no potential for radioactive pollution. Geothermal modes of generating electricity do share with fossil-fuel and nuclear modes the potential for thermal pollution; indeed, the amount of waste heat per unit of electricity generated is higher for geothermal than for either nuclear or fossil-fuel modes, owing to the low turbine efficiencies at the low geothermal steam pressures. Geothermal effluents, as well as being warm, commonly are mineralized and thus present a chemical pollution hazard to surface or ground waters. Accordingly, most if not all proposed geothermal developments in the United States plan to dispose of unwanted effluent by reinjection into the geothermal reservoir.

Other insults to the environment that are inherent in geothermal development are in large part controllable at reasonable costs. These include noise (drilling, testing, and production), gaseous emissions (particularly H_2S), and industrial scars. Intensive geothermal exploitation may cause subsidence, due either to fluid withdrawal (Hunt, 1970) or to thermal contraction of rock as heat is withdrawn. Reinjection of water in fault zones may increase the incidence of earthquakes, by a mechanism similar to that demonstrated for the Rocky

Mountain Arsenal well in Colorado by Healy, Rubey, Griggs, and Raleigh (1968).

Bowen (1973) correctly pointed out that "To understand properly the impact of the production of electric power on the environment, it is necessary to evaluate more than just the power plant, whether it is geothermal, nuclear, or fossil fueled; the entire fuel cycle from mining, processing, transportation, and the disposal of spent wastes must be considered." When viewed in this light, the environmental impact of geothermal generation does indeed appear to be minor compared with fossil-fuel or nuclear generation. The environmental impact of geothermal generation is restricted to the generating site, whereas much of the environmental impact of other modes of generating takes place at other sites (mines, processing plants, disposal sites) and is commonly neglected in the evaluation of environmental impact of a power plant.

GEOLOGIC ENVIRONMENTS

Geothermal reservoirs are the "hot spots" of larger regions where the flow of heat from depth in the earth is about 1½–5 times the worldwide average of 1.5×10^{-6} calories per square centimeter per second. Such regions of high heat flow commonly are zones of young volcanism and mountain building and are localized along the margins of major crustal plates (Muffler and White, 1972, fig. 1). These margins are zones where either new material from the mantle is being added to the crust or crustal material is being dragged downward and "consumed" in the mantle. In both situations, molten rock is generated at depth and moves buoyantly upward into the crust. The resultant pods of igneous rock provide the heat that is then transferred by conduction to the convecting systems of meteoric water.

There are two major types of geothermal systems: (1) hot water (White, 1970, 1973) and (2) vapor dominated ("dry steam") (White and others, 1971; Truesdell and White, 1973; White, 1973). In a hot-water geothermal system, the fluid in the rock at depth is water alone. Steam is produced by boiling as the fluid moves up a well to the surface, and a mixture of steam and water is produced at the surface; the water must be removed from the steam before the steam is fed to a turbine. Vapor-dominated geothermal systems, on the other hand, contain both water and steam in the reservoir at depth. With decrease in pressure upon production, heat contained in the rock dries the fluids first to saturated and then to superheated steam, which can be piped directly into a turbine. Among geothermal systems discovered to date, hot-water systems are perhaps 20 times as common as vapor-dominated systems (White, 1970).

Potentially recoverable geothermal resources also occur in some regions where the normal heat flow of the earth is trapped by insulating impermeable clay beds in a rapidly subsiding geosyncline. For example, along the gulf coast of the United States, temperatures of 150°C–273°C are found at depths of 4–7 km in geopressured zones (Jones, 1970). Waters in these geopressured zones are not circulating meteoric water; they are produced by compaction and dehydration of the sediments themselves.

RESOURCES AND PROBLEMS

Estimates of the geothermal resources of the United States and of the world differ by as much as six orders of magnitude. White (1965, p. 14) stated that "existing worldwide utilization equivalent to about 1 million kw * * * probably can be increased at least 10 times [that is, to 10^4 Mw] under present economic conditions and maintained for at least 50 years." Banwell (1967, p. 155) estimated a potential heat production of 2×10^9 kg-cal/sec from geothermal energy associated with "Pacific type volcanism." At 14 percent thermal efficiency, this rate of heat production could sustain electrical generating capacity of about 10^6 Mw. Rex (1971a, p. 54) stated that he and his colleagues " * * * are estimating the western [conterminous] U.S. geothermal potential from 10^5 to 10^7 megawatts." White (1965) and Muffler and White (1972) estimated that the world geothermal resource to a depth of 3 km for electrical generation by proven techniques is approximately 2×10^{19} calories (equivalent to 58,000 Mw for 50 yr). Rex (1972a) stated that " * * * the present recoverable [geothermal] resource for the western third of the continental United States, excluding Alaska, is of the order of 10^5 megawatt-centuries. This figure could be expanded by another factor of 10 by the inclusion of the eastern two-thirds of the United States and another factor of 10 [that is, to 10^{10} megawatt-centuries] by improvements in technology." [1] John Banwell and Tsvi Meidav (oral presentation, Ann. Mtg. Am. Assoc. Adv. Sci., Philadelphia, 1971; ms. supplied by Tsvi Meidav) stated that "The geothermal energy reserves of the world are orders of magnitude greater than the total reserve of any other form of fossil energy."

The wide variance among these resource estimates reflects several factors—predominantly, the defini-

[1] If one assumes 14 percent thermal efficiency (as in Rex, 1972b), this electricity is produced from 4.93×10^{25} cal. or approximately eight times the estimate of White (1965, p. 2) for the total heat stored under the United States to a depth of 10 km.

tion of the term "resources" as used by the respective authors. Schurr and Netschert (1960, p. 297) stated:

> The "resources" of a mineral raw material may be defined according to any technical and economic criteria that may be considered relevant and appropriate. The resources consist of that part of the resource base (including reserves) which seem likely to become available given certain technologic and economic conditions. * * * Whether any particular definition of resources is useful depends on the context in which it is to be used and the possibility and need for expressing it quantitatively. It is essential in any event that an explicit definition always be given in conjunction with the use of the term.

Particularly for geothermal resources, it accordingly is incumbent upon any author to define his usage of "resources" and to state explicitly his assumptions. Most authors are seriously remiss in this regard, and their resource estimates must therefore be viewed with skepticism.

The "resource base" was defined by Schurr and Netschert (1960, p. 297) as all of a given material present in the earth's crust, whether its existence is known or unknown and regardless of cost considerations. For geothermal resources, the "resource base" is therefore all of the heat in the earth's crust, presumably measured from O°K (= —273.15°C). For obvious practical reasons, heat below mean surface temperature of the earth (about 15°C) is excluded from consideration, and the geothermal resource base may be considered as all heat above 15°C in the earth's crust. Quantification of the geothermal resource base depends on the definition of the term "crust," the estimate of the dimensions of the crust, the three-dimensional distribution of temperature within the crust at any particular moment, and the heat flux between the mantle and the crust and between the crust and the atmosphere.

What proportion of the geothermal resource base should be considered as a resource? This proportion depends on evaluation of the following factors, many of which are interdependent:

1. Depth of extraction, which is dependent on the technology and economics assumed. White (1965) gives estimates of geothermal resources to depths of 3 km, the deepest geothermal well drilled to date, and 10 km, the deepest well likely to be drilled in the foreseeable future.
2. Three-dimensional temperature distribution to the depth assumed.
3. Specific heat distribution; a convenient approximation presented by White (1965) is based on the fact that most earth materials have nearly equal volumetric specific heats.
4. Porosity, effective porosity, specific yield, and permeability.
5. Physical state of the fluid in the reservoir (water or steam).
6. Available technology.
7. Economics of various possible uses.
8. Governmental policy with respect to societal needs, environmental constraints, and availability of other forms of energy.

Many physical factors that control the distribution of heat to any given depth can be evaluated, at least rudely (White, 1965, 1973; Banwell, 1967; Rex, 1971b; Muffler and White, 1972). More tenuous are the assumptions of technology, economics, and governmental policy. These assumptions are critical to geothermal resource estimation, and differences (explicit or implicit) among them are in great part responsible for the vast range in magnitude among geothermal resource estimates.

Geothermal reserves (defined as those resources recoverable at present at costs competitive with alternative forms of energy) are clearly limited if one considers only generation of electricity. For the generation of electricity using proved and demonstrated technology, the geothermal reservoir must have a temperature of at least 180°C; at lower temperatures the quantity of flash steam is inadequate (fig. 28). Reservoirs at this or higher temperature, at recoverable depths, and with adequate

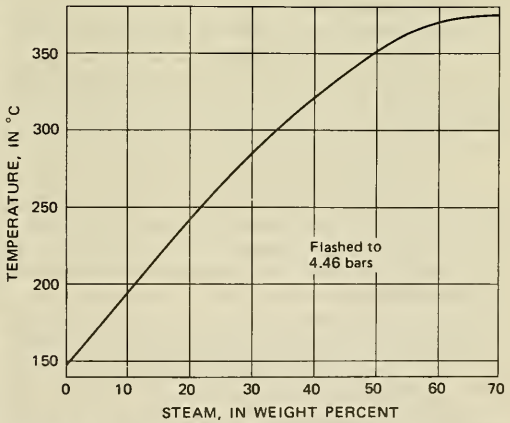

FIGURE 28.—Weight percent of steam produced by flashing water at various temperatures to a turbine inlet pressure of 50 lb in^{-2} gauge (James, in press). Graph calculated from data given in tables 1 and 2 of Keenan and others (1969).

productivity are unlikely to be abundant. White (1965) estimated resources recoverable as electricity to 3 km to be 2×10^{19} calories ($=2.32 \times 10^{13}$ kwhr). This energy is less than one ten-millionth of the total amount of heat above 15°C in the outer 10 km of the earth (White, 1965, p. 2).

Utilization of a greater proportion of the heat stored in the outer 10 km of the earth depends on achieving one or more of the following items:

1. Technological advances that would allow electrical generation from low-temperature reservoirs.
2. Breakthroughs in drilling technology that would permit low-cost drilling of holes to depths greater than 3 km.
3. Development of techniques of artificial stimulation that would increase the productivity of geothermal reservoirs.
4. Expansion of the use of low-grade geothermal resources for such purposes as space heating, product processing, agriculture, and desalination.

Several of these breakthroughs may occur in the reasonably near future; if they do, the recoverable resource estimates of White (1965) will have to be revised upward to reflect the major changes in basic assumptions. Four possible breakthroughs deserve specific mention:

1. Much attention is currently being paid to the possible generation of electricity from low-temperature geothermal waters, using a system whereby the geothermal heat is used in a heat exchanger to boil a secondary fluid such as isobutane or freon. This low-boiling fluid (as a gas) drives a turbine, is condensed, and then returns to the heat exchanger (Jonsson and others, 1969). A generating unit based on the heat-exchange principle and using intake water at 81°C is reported to be in pilot operation at Paratunka, Kamchatka, U.S.S.R. (Facca, in press). U.S. industry interest in this generating mode is high (Anderson, 1973), although no pilot or prototype plant has yet been built.
2. Successful demonstration of the technical feasibility of geothermal self-desalination (U.S. Bur. Reclamation, 1972) could greatly enhance the economic position of geothermal resources. Particularly in water-short parts of the world, geothermal energy may be the preferable energy source for desalination, either of the geothermal brine itself or of other saline waters near the geothermal development.
3. Research at the LASL (Los Alamos Scientific Laboratory) has recently been focused on the development of a nuclear drill that would bore holes in rock by progressive melting rather than by chipping, abrading, or spalling (Smith, 1971). If development of this "nuclear subterrene" is successful and its use is relatively inexpensive, extraction of geothermal energy from depths as much as 10 km may become feasible.
4. One possible application of the nuclear subterrene proposed by LASL is to drill to depths greater than 5 km in regions where temperatures may be abnormally high but where permeability is low. LASL proposes to hydrofac the hot rock to increase permeability and expects that extraction of heat by water circulated through the crack will result in thermal-stress cracking and a continuously enlarging crack system (Aamodt and Smith, 1973; Harlow and Pracht, 1972). Geothermal reservoir stimulation by various methods (including nuclear devices) was recently the subject of a symposium of the American Nuclear Society (Kruger and Otte, 1973).

Another confusing aspect of geothermal resource estimation involves the units of energy in which the estimates are expressed by various authors. Geothermal energy is heat, and the resource and reserve estimates therefore should be expressed in calories, joules, or Btu's. But historically the major use of geothermal energy has been to generate electricity, and resource estimates commonly have been expressed in units of electrical energy (kilowatt-hours or megawatt-years) or in terms of installed electrical capacity (kilowatts or megawatts). In converting from calories to kilowatt-hours, however, one cannot blindly use the energy conversion factors given in standard tables (for example, Handbook of Chemistry and Physics). These conversion factors, although mathematically and physically accurate, do not take into account the thermodynamic inefficiencies in converting heat to electricity via a turbine and generator. For example, in units 3 and 4 at The Geysers, Calif. (a vapor-dominated geothermal system), only 14.3 percent of the energy delivered to the turbine is actually converted to electricity (Bruce, 1971). Almost all the remaining 85.7 percent is discharged as heat to the atmosphere, with only a small fraction of heat being returned to the reservoir in condensate from the cooling towers.

The best fossil-fuel generating plants in the United States have a thermal efficiency of about

40 percent; the best nuclear plants, about 33 percent (U.S. Library of Congress, 1970). The relatively high efficiencies of these generating modes compared with geothermal modes are mainly due to the much higher temperatures and pressures of steam input.

Any system that generates electricity from heat has an efficiency limited by the second law of thermodynamics. An ideal (Carnot) engine will have a thermal efficiency equal to $1-(T_1/T_2)$, where T_1 is the final temperature, in degrees Kelvin, and T_2 is the initial temperature, in degrees Kelvin (Hossli, 1969). Thus, for geothermal generation (as at The Geysers) where $T_1 = 80°F$ (299.8°K) and $T_2 = 355°F$ (452.6°K) (Barton, 1972, fig. 4), the maximum theoretical efficiency is $[1-(299.8/452.6)](100) = 33.9$ percent. For a fossil-fuel plant at $T_1 = 100°F$ (311°K) and $T_2 = 1{,}000°F$ (811°K), the maximum theoretical efficiency would be 61.6 percent.

The overall generating efficiency of an installation at a hot-water geothermal field is even less, owing to the fact that under existing technology only the steam can be utilized in a turbine. In a hot-water system at 260°C (like Wairakei, New Zealand), the fluid delivered to the power plant at a turbine inlet pressure of 50 lb in^{-2} gauge (4.46 bar absolute) is by weight 24 percent steam and 76 percent water. Fifty-nine percent of the produced heat is in the steam, and 41 percent, in the water. Accordingly, the overall thermal efficiency of a 260°C hot-water geothermal installation is approximately (59 percent) (14.3 percent) $\cong$ 8 percent.

Geothermal resources cannot be expressed in kilowatts or megawatts unless the assumed life of the system and the plant factor (for geothermal generation usually assumed to be 8,000 hr yr^{-1}) are also specified. Kilowatts and megawatts are units of electrical capacity, not electrical energy, and thus are a function of not only the size of the geothermal resource but also the rate of production. The rate of production depends on the economics of the particular situation; production has to be held to a level that will allow the capital facilities to be amortized before the field is exhausted. The largest geothermal field imaginable presumably could be exhausted in 1 year, at prohibitive economics. More reasonable assumptions for field life fall between 25 and 50 years.

Even if one restricts resource discussion to heat and thus avoids the possible ambiguity of electrical units, one must be careful to specify whether the heat considered is total heat in a specified volume of ground, heat in the fluid phase only, heat that actually can be extracted from the ground, or heat actually delivered to a turbine.

To illustrate these differences, consider a hypothetical hot-water geothermal system to a depth of 3 km, with temperatures controlled by the boiling-point curve to a base temperature of 260°C. I assume a rock particle density of 2.6 g cm^{-3}, a rock specific heat of 0.2 cal g^{-1} $°C^{-1}$, and all calculations referred to 15°C. Using steam table data (Keenan and others, 1969) and the boiling-point curve for pure water at sea level (Haas, 1971), one can calculate incrementally that the heat contained in the geothermal system at temperatures less than 260°C (that is, at depths shallower than 0.5518 km) is 6.3×10^{16} cal km^{-2}. The heat stored at 260°C from 0.5518 to 3.0 km is 34.0×10^{16} cal km^{-2}. Therefore, the total heat in the geothermal system above 15°C is approximately 40.3×10^{16} cal km^{-2}.

The amount of heat remaining after exploitation perhaps can be approximated by assuming that the geothermal system drops to a base temperature of 180°C; the calculations are similar to those just shown. The heat withdrawn during exploitation is then the difference between the heat at the initial state (40.3×10^{16} cal km^{-2}) and the heat at the final (depleted) state (28.5×10^{16} cal km^{-2}), or 11.8×10^{16} cal km^{-2}. This figure is undoubtedly too high, perhaps by a factor of 2, owing to inefficient extraction because of impermeable rock, insufficient number of drill holes, and drilling spacing that is not optimum. Therefore, the heat actually delivered to the surface wells will be approximately 5.9×10^{16} cal km^{-2}, about 15 percent of the heat actually stored in the initial geothermal system above 15°C. Taking into account the 14.3 percent thermal efficiency of generation and the heat wasted in hot water (41 percent), we find that only 1 percent of the heat contained in this hot-water geothermal system can be converted into electricity.

The amount of heat and water recharge assumed to enter the system from greater depths should also be specified in the estimation of the geothermal resources or reserves of any area. Calculations such as the above do not take into account the possibility of recharge, and therefore give only a minimum figure for the heat that may ultimately be derived from a geothermal system. At Wairakei, New Zealand, recharge is significant. Hunt (1970), using precise gravity and leveling techniques at various times during exploitation of the field, has shown that about 20 percent of the water drawn off from the Wairakei field from 1961 to 1967 was replaced by recharge. Although recharge is clearly a significant factor in geothermal reserve estimations, its

quantitative importance cannot be evaluated without making some estimate of the rate of exploitation of the reservoir. If exploitation is very rapid, recharge will have little significance, but if exploitation is very slow, recharge will be significant; thus, establishment of a steady balance between extraction and recharge (both heat and water) may permit the geothermal system to be exploited indefinitely.

The geothermal resources of the world, therefore, lie somewhere between 2×10^{19} cal (White's 1965 estimate of potential reserves to 3 km recoverable as equivalent electrical energy using present technology) and $5\text{–}10\times10^{25}$ cal (calculated from Rex, 1972a). Of these geothermal resources, perhaps 5–10 percent are in the United States (White, 1965). The differences among the various resource estimates will not be resolved until there is (a) better knowledge of the distribution of geothermal energy in the earth's crust, (b) clarification of the technological limitations upon geothermal resource exploitation, and (c) definition of uses.

PROSPECTING TECHNIQUES

The first step in reconnaissance geothermal exploration involves outlining broad regions where the heat flow is significantly greater than 1.5×10^{-6} cal cm^{-2} sec^{-1} (for example, Sass and others, 1971). Most of these regions of high heat flow are in zones of young volcanism and tectonic activity, and most are characterized by abundant hot springs.

Techniques for identifying potentially economic concentrations of geothermal energy within broad regions of high heat flow are not well developed. Important considerations include distribution of hot springs, evaluation of volcanological and tectonic setting, and chemical analysis of hot-spring fluids. In particular, the content of silica (Fournier and Rowe, 1966) and the ratios of sodium, potassium, and calcium (Fournier and Truesdell, 1973) provide information about the minimum subsurface temperature to be expected.

Several geophysical techniques have proved useful in the final delineation of geothermal targets (Combs and Muffler, 1973; Banwell, in press). Of these techniques, perhaps the most unambiguous is the direct measurement of temperature gradients at depths of 25–100 meters (Combs, 1971; Burgassi and others, 1970). Temperature measurements at shallower depths, however, can be very misleading, owing primarily to the effects of seasonal changes in temperature and to the shallow movement of ground water (Banwell, in press). Thermal infrared surveys detect surface temperature anomalies, but these anomalies can be caused by many factors other than geothermal heat flow (Banwell, in press; Watson and others, 1971).

Several techniques that measure the electrical conductivity at depth have had great success in geothermal exploration. The conductivity at depth varies directly with temperature, porosity, salinity of interstitial fluid, and content of clays and zeolites. All these factors tend to be higher within good geothermal reservoirs than in the surrounding ground, and consequently the electrical conductivity in these geothermal reservoirs is relatively high. Electrical conductivity at depth can be measured by electrical (galvanic) or electromagnetic (inductive) methods. Among the electrical techniques, only direct-current methods are reliable, owing to skin effects attendant to alternating-current methods; direct-current electrical arrays commonly used are Wenner, Schlumberger, and dipole-bipole (Banwell and Macdonald, 1965; Hatherton and others, 1966; Risk and others, 1970; Macdonald and Muffler, 1972; Zohdy and others, 1973). Electromagnetic methods (audiofrequency magnetotellurics, electromagnetic coil surveys, and loop-loop or wire-loop induction surveys) have certain theoretical advantages (Keller, 1970; Harthill, 1971) and are becoming more widely used.

Passive seismic methods are proving of use in locating fractured and permeable zones in geothermal areas. Microearthquakes at relatively shallow focal depths are concentrated along fracture or fault zones in many geothermal areas (Ward, 1972; Ward and Björnsson, 1971; Hamilton and Muffler, 1972). In addition, some geothermal areas appear to have a high level of seismic ground noise (Whiteford, 1970); analysis of the areal distribution of this noise may outline prospective zones of geothermal production (Goforth and others, 1972).

Several other geophysical techniques have proved useful in special circumstances. Gravity surveys may in some areas define positive anomalies that are caused by alteration or metamorphism of subsurface rock (Hochstein and Hunt, 1970; Biehler, 1971), but in other areas they may define a negative anomaly that may represent an intrusive mass at depth (Calif. Div. Mines and Geology, 1966). Magnetic surveys in some areas define negative anomalies that are caused by alteration of magnetite to pyrite (Studt, 1964), but in other areas they define positive magnetic anomalies that are caused by intrusions of magnetic igneous rock (Griscom and Muffler, 1971). Active (explosion) seismology is useful in defining subsurface geologic structure (Hochstein and Hunt, 1970; Hayakawa, 1970), and analysis of seismic attenuation across geothermal

areas may someday become useful in geothermal exploration (Hochstein and Hunt, 1970).

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GOLD

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ABSTRACT OF CONCLUSIONS

Most of the world's gold reserves, estimated at 1 billion ounces, are in South Africa, and that country will continue to produce two-thirds of the world's gold for many years. The U.S.S.R. is thought to have a large part of the remainder, and no other country has more than a few percent of the reserves. Official world gold currency reserves are about 1.3 billion ounces, and a somewhat smaller amount is hoarded; both reserves and hoards may become sources of industrial gold, the first by government decision, the second by a sufficient rise in the price of gold.

United States nonmonetary consumption of gold has been three to four times domestic production for several years, and the United States is unlikely to become self-sufficient in gold in the foreseeable future. United States gold reserves of a few tens of millions of ounces are mainly in the Homestake (S. Dak.) and Carlin and Cortez (Nev.) gold deposits and in copper deposits, such as Bingham, Utah, which produce byproduct gold. U.S. gold resources are large but in general very low grade, and most placer deposits pose insurmountable technologic problems at present. Deposits as yet undiscovered that are most likely to provide new gold production are those of disseminated gold, similar to Carlin and Cortez, which were overlooked in early prospecting.

INTRODUCTION

Gold is a yellow metal that has a density of 19.3 grams per cubic centimeter (nearly twice that of lead and exceeded only by some of the platinum metals and rhenium) and that is soft, very malleable and easily shaped, and highly resistant to corrosion and tarnish. Because of its workability, beauty, durability, and common occurrence as native metal, gold was one of the first metals used by man. Over the centuries it has been a principal medium of international monetary exchange, and its physical properties have made it prized for jewelry and other adornments. Gold has traditionally been equated with wealth, and the lore of lost gold mines and hidden pirate hoards cannot be matched by that of any other commodity. Even today gold is sought by the weekend prospector in the hope of striking it rich, as a very few of his predecessors did a century ago.

Gold is known to have been mined in substantial amounts for at least 6,000 years, probably first in Egypt, where gold objects appeared as early as 4,000 B.C. (Sutherland, 1960, p. 25). Various estimates of the amount of gold mined since the discovery of

America converge at about 2.5 billion ounces (see table 50 for weights and measure) (Wise, 1964, p. 9; Green, 1968, p. 14; Kavanagh, 1968, p. 553; Park, 1968, p. 121; Ageton, 1970, p. 574), and a reasonable guess about earlier production leads to an estimated total production through world history of about 3 billion ounces (Kavanagh, 1968, p. 553). Because of its indestructibility, intrinsic value, and appeal, gold endures. Some undoubtedly was lost in sunken ships, some has been entombed with its owners, and some was hidden by people long dead, but a very large part of all that was ever produced probably can be accounted for. Official monetary reserves are about 1.3 billion ounces (U.S. News & World Report, 1972, p. 21). The difference between this amount and the estimated world total production is about 1.7 billion ounces; this figure, less whatever gold has been irretrievably lost, gives an order of magnitude for the quantity of gold in jewelry, coin collections, museums, church adornments, electronic equipment, capitol domes, teeth, and, above all, hoards in the form of bars or coins. The amount is enormous, but some perspective may be gained from the realization that during 1966–68 alone, all newly mined gold, about 120 million ounces exclusive of the U.S.S.R., plus about 66 million ounces from non-Communist official reserves—that is, a total of 186 million ounces—passed into private holdings (Hoyt, 1971, p. 522, 538). Between 1941 and 1968, an estimated 550 million ounces of gold came under private control (Busschau, 1967, p. 21; Park, 1968, p. 114). Park (1968, p. 121–122) estimated that nearly 550 million ounces of gold are held in hoards alone. By way of contrast, U.S. monetary reserves of gold at the end of 1971 totaled only 291.6 million ounces (U.S. Dept. Interior, 1972, app. 1, p. 103).

TABLE 50.—*Equivalent weights and measures for gold*

[All data in this report are in Troy ounces or metric units, such as grams or tons. g, grams; dwt, pennyweights; oz, ounces; ppm, parts per million; ppb, parts per billion]

WEIGHTS AND MEASURES

Weight or measure	*Equivalent*
1 Troy ounce	31.1 g
	20 dwt
1 metric ton	10^6 g
	32,150 oz
	1.1 short ton
1 ppm	1 g per ton
	0.032 oz per ton
1 ppb	0.001 g per ton

PRICES

Price per ounce	*Value of 1 g*
$35	$1.12
40	1.29
45	1.45
50	1.61
70	2.24
100	3.22

USES

Gold has traditionally been the principal medium of international monetary exchange, but its role has undergone profound change in recent years. From 1934 to 1972 the United States maintained full convertibility of the dollar to gold at a fixed rate of $35 per ounce. Increasing balance-of-payments deficits starting after World War II, and rising industrial consumption of gold, caused a steady drain on U.S. monetary reserves of gold. In March 1968, agreement was reached among seven major monetary nations (Belgium, Great Britain, Italy, Netherlands, Switzerland, United States, and West Germany) to discontinue open-market buying or selling of gold but to continue intergovernment transactions at the same price of $35 per ounce. As a result of this agreement, the U.S. Treasury stopped selling gold for industrial use, thus slowing down the drain on official reserves. However, the balance-of-payments deficits continued, and on August 16, 1971, the U.S. Government suspended convertibility. On December 18, 1971, the Group of Ten nations (the same countries as above, less Switzerland and plus Canada, France, Japan, and Sweden) agreed to raise the official price of gold to $38 per ounce, and this agreement was signed by the President of the United States on April 3, 1972. After establishment of a free market for gold in 1968, the price fluctuated between $35 and $45 per ounce until early 1972, when the price started to rise sharply, and it reached $70 per ounce in early August 1972. These events are certain to have a significant effect on the future monetary role of gold, but their full impact cannot be predicted at this time.

Gold has a long history of use in the manufacture of jewelry and related articles and in dentistry, and more recently it has achieved wide industrial use, particularly in the electronics and computer industries. U.S. consumption of gold in industry and the arts has been 6–7 million ounces annually during 1967–72, and in 1971 it was distributed as follows: jewelry and arts, 60 percent; dentistry, 11 percent; industry, 29 percent (U.S. Bur. Mines, 1972, p. 60). All these nonmonetary uses of gold are rising steadily—in the arts and dentistry because of population growth and increasing affluence, and in industry for fabrication of semiconductors, printed circuits, connectors, and other microcomponents for computer and space application. Nonmonetary use of gold in the rest of the world is estimated at three to four times that of the United States, but distribution of consumption among various uses is not accurately known.

Gold has no entirely suitable substitute for any of its major uses. Platinum is a substitute in jewelry but is more costly and lacks the color and appeal of gold; silver is not sufficiently tarnish resistant. Various stainless alloys are usable in dentistry but are more difficult to fabricate. Silver can be substituted in many electronics applications but is much less corrosion resistant and somewhat less ductile. Nevertheless, gold can be replaced or its use deferred in all its main areas of utilization, and in this sense it is not as vital an industrial commodity as, for instance, copper.

EXPLOITATION

World gold production is dominated by a single country, the Republic of South Africa (fig. 29).

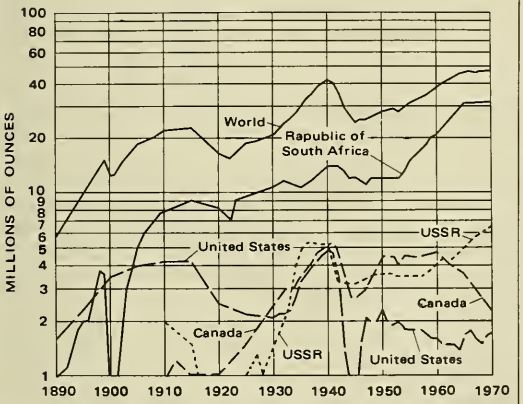

FIGURE 29.—World gold production, 1890–1970. Data for U.S.S.R. are from U.S. sources; production since 1936 is estimated. Estimates from European and South African sources for annual production of U.S.S.R. since about 1945 are higher than those shown and range from 7 to 10 million ounces or more.

South Africa has produced about 37 percent of the estimated 2.5 billion ounces of gold mined since the discovery of America, and in the last decade it has annually produced about two-thirds of the world total output. Current production from that country is about 31 million ounces of gold annually. By contrast, only three other countries produced more than a million ounces in 1970: the U.S.S.R., 6.5 million ounces (estimated); Canada, 2.3 million ounces; and the United States, 1.8 million ounces. Other countries that produce more than 100,000 ounces of gold annually are, in approximate decreasing order of output, Australia, Ghana, Philippines, Rhodesia, Japan, Colombia, Nicaragua, Brazil, Mexico, Zaïre, Peru, India, and Fiji Islands.

Gold production of the Communist nations can only be estimated because figures are not released by them; Russian production, for instance, has not been officially reported since 1936. The U.S.S.R. is known to be a major gold producer, and for much of the 19th century it led the world in gold output. From the discovery of America until 1970, production from the U.S.S.R. is estimated between 290 and 350 million ounces, approximately the same as that of the United States (315 million oz) (Emmons, 1937, p. 329; U.S. Bur. Mines, 1932–71; Busschau, 1967, p. 21). North Korea is estimated to produce 160,000 ounces annually, and mainland China, 50,000–60,000 ounces annually. Bulgaria, Czechoslovakia, Hungary, and Rumania are minor producers.

U.S. estimates of annual U.S.S.R. gold production made from 1940 to 1963 showed a gradual increase from about 4 million ounces in the early 1940's to a high of 12.5 million ounces in 1963. In 1964 these estimates were drastically revised downward to a low of 3.2 million ounces in 1943 and a high of only 4.4 million ounces in 1963 (U.S. Bur. Mines, 1965, p. 530–531; Green, 1968, p. 75–76). Production from the U.S.S.R. during 1967–72 has been estimated by the U.S. Bureau of Mines at 5–7 million ounces annually, and some other estimates have been as much as 50 percent higher. Russian sales of gold ranged from 2 to 16 million ounces annually during 1950–65, and in the period 1963–65 they averaged more than 14 million ounces per year (Busschau, 1967, p. 21). From 1966 to 1970, very little gold was sold by Russia, but gold sales were resumed in 1971.

U.S. gold production for the last 25 years has generally been 1.5–2 million ounces annually (fig. 30).

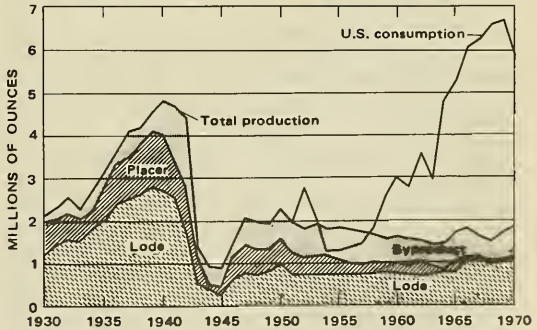

FIGURE 30.—U.S. gold production, 1930–70—from lode, placer, and byproduct sources—and U.S. gold consumption, 1951–70.

About 60 percent of current U.S. production comes from lode deposits, and 40 percent is a byproduct from the refining of other metals, principally copper. Placer deposits, once a major source of gold in the United States, are now only a very minor source.

In recent years, consumption of gold in the United States has been three to four times domestic production of new gold. The difference between the amount consumed and the amount produced is made up by reclaimed scrap gold (2.3–3 million oz annually (U. S. Bur. Mines, 1972, p. 60)), by releases from U.S. Treasury stocks (until 1968), and by imports, mainly from Canada. The United States thus is far from being self-sufficient in gold, and it is unlikely to become so in the foreseeable future.

GEOLOGIC ENVIRONMENT

GEOCHEMISTRY

Gold is a rare element—at least 70 of the naturally occurring elements are more abundant, most of them at least an order of magnitude more abundant, than gold (Rankama and Sahama, 1950, p. 39–40; Mason, 1966, p. 45–46; Krauskopf, 1967, p. 639–640; Lee and Yao, 1970, p. 782).

Estimates of abundance of gold in the earth's crust made during the last 50 years range from 0.001 ppm (parts per million) to 0.006 ppm; as analytical methods have improved, earlier estimates have been reduced. A reasonable estimate of crustal abundance based on modern analyses is 0.003–0.004 ppm, or about 1 g (gram) per 300 metric tons (Jones, 1968, p. 3; Lee and Yao, 1970, p. 782). Gold is more abundant in mafic than in felsic igneous rocks (Gottfried and others, 1972, p. 8, 21) and apparently is somewhat more abundant in sedimentary than in igneous rocks and in sandstone than in other sedimentary rocks, although data are sparse (Jones, 1969).

Gold is much more abundant in the iron-rich meteorites than in rocks of the earth's crust, as shown by the following data from Jones (1968, p. 1–3). The iron meteorites, or siderites, contain as much as 8 ppm gold, but the average ranges from 0.67 to 1.3 ppm, or 150–300 times as much as the earth's crust. The siderolites, or stony iron meteorites, contain about the same amount of gold as the siderites. The chondritic stony meteorites contain 0.15–0.27 ppm gold, 40–70 times as much as crustal rocks, whereas achondritic meteorites have about the same gold content as the earth's crust. The earth's core is believed to be chemically similar to the iron meteorites, and the earth's mantle, similar to the chondritic stony meteorites; so most of the earth's gold is probably locked up below the earth's crust. However, rocks that are believed to have been part of the mantle and that are now exposed at the earth's surface do not show notable enrichment in gold; the most iron rich of these, the dunites, contain only about twice the average gold content of the crust (Jones, 1969, p. 15, tables 4, 5).

The abundance of gold in the oceans appears to vary appreciably from ocean to ocean and within a given ocean; two recent estimates of average gold content are 0.011 ppb (part per billion) (1 g per 90,000 tons of sea water) (Rosenbaum and others, 1969) and 0.05 ppb (1 g per 20,000 tons of sea water) (Jones, 1970, p. 1–3).

Bedrock deposits of gold that have been mined profitably have contained gold in amounts ranging from 0.05 to 1 ounce or more per ton, but the average gold content appears to be in the range of 0.3–0.5 ounce per ton. Ore being mined at present at the three largest gold mines in the United States (Homestake, S. Dak.; Carlin and Cortez, Nev.) averages about 0.3 ounce per ton, or about 10 ppm. This gold content represents a concentration of 2,500–3,000 times the average crustal abundance. This ratio of concentration, which is in a very general way a measure of the likelihood of occurrence of an economic concentration of an element (the higher the ratio of concentration, the less the likelihood that concentrations of the requisite size and grade will be formed), is one of the highest needed to produce an economic mineral deposit.

In ore deposits, gold is commonly associated with pyrite and sulfide minerals of silver and copper even though it does not form a separate sulfide mineral. All gold ores contain some silver, many ores that are predominantly of silver contain appreciable quantities of gold, and copper ores produce the bulk of byproduct gold.

Gold deposits are found in so great a variety of rocks as to almost preclude generalizations about association of gold with particular rock types. Nevertheless, gold deposits occur more commonly with felsic or intermediate igneous rocks than with mafic or ultramafic types, and more commonly in siliceous or aluminous sedimentary or metamorphic types than in carbonate rocks (however, the host rock at the recently discovered Carlin and Cortez gold deposits in Nevada is a silty dolomitic limestone).

Gold is extremely inert in natural environments at the earth's surface, and during weathering and decomposition of rocks it is little affected. Thus, it may be residually concentrated at the weathering site or transported in the native state and concentrated locally along with other highly resistant min-

erals in placer deposits. Gold is soluble in hydrochloric acid in the presence of manganese dioxide but is appreciably so only at concentrations of acid so high as to occur only rarely in nature (Krauskopf, 1967, p. 523–526).

MINERALOGY

Gold occurs mainly as native metal, always alloyed with variable amounts of silver and other metals, mainly copper and iron. Other than native gold, the only important gold minerals are the tellurides, composed of gold or gold plus silver, copper, or lead combined with tellurium; calaverite ($AuTe_2$) and sylvanite ($[Au,Ag]Te_2$) are the most common of these minerals. Other gold minerals are rare. Gold also occurs in small amounts in many minerals, generally less than 5 ppm in sulfide minerals, and less than 1 ppm in other minerals; however, as much as 500 ppm has been reported from sphalerite (zinc sulfide) (Jones and Fleischer, 1969, p. 11).

TYPES OF GOLD DEPOSITS

Gold occurs in many and varied geologic environments, which are grouped into seven broad categories in this report.

Historically, the most productive general types of deposits have been gold-quartz lodes and a subcategory of these, the epithermal ("bonanza") deposits (mainly in the North American Cordilleran region); geologically young placers; and ancient (fossil) placers. Other types are marine placers; bedrock deposits of disseminated gold, a type represented by several recent discoveries in Nevada; and deposits of other metals or minerals which produce gold only as a byproduct (Internat. Geol. Cong., 1930; Lindgren, 1933; Emmons, 1937; Cooke, 1946; Canadian Inst. Mining and Metall., 1948; Bateman, 1950; Commonwealth Mining and Metall. Cong., 6th, 1957; Commonwealth Mining and Metall. Cong., 8th, 1965; De Kun, 1965; Koschmann and Bergendahl, 1968; Canada Geol. Survey, 1970; Park and MacDiarmid, 1970; Roberts and others, 1971).

GOLD-QUARTZ LODES

Examples of gold-quartz lodes are Mother Lode–Grass Valley, Calif.; Homestake, S. Dak.; Central City, Colo.; Alaska Juneau–Treadwell, Alaska; Porcupine and Kirkland Lake–Larder Lake, Ontario, Canada; Morro Velho, Minas Gerais, Brazil; Kolar, Mysore, India; Kalgoorlie, Western Australia; Bendigo-Ballarat, Victoria, Australia; Ashanti, Ghana; the Bulawayo and Hartley belts, Rhodesia; and the Kilo and Moto districts, Zaïre. This category comprises a wide variety of deposits, but these are essentially hydrothermal veins of quartz and gold that either replace wallrock (Homestake) or fill open spaces along fracture zones (Mother Lode). They were formed at great depths below the earth's surface and persist to depths of thousands of feet below the present surface, and most of them are enclosed in Precambrian rocks and are of Precambrian age. Alteration of wallrocks ranges from slight (Homestake) to widespread and pervasive (Alaska Juneau). The gold content of ores mined ranges from about 0.3 to about 0.6 ounce per ton; only rarely has much ore containing more than 0.6 ounce per ton been found, and conversely in only a few mines has ore containing as little as 0.1 ounce per ton been mined profitably.

The size of the gold-quartz lodes varies greatly, and data on individual deposits or mines are difficult to obtain for many of the great gold-mining districts. Many mines have produced at least 1 million ounces (North Star and Empire mines, Grass Valley, Calif.); an appreciable number have yielded 2–5 million ounces (Alaska Juneau; Brownhill-Oroya and probably several other mines at Kalgoorlie, as well as at Bendigo and Ballarat, Australia); a few have produced 5–20 million ounces (Hollinger, McIntyre, and Dome mines, Porcupine, Ontario; Kirkland Lake zone, including the Lake Shore and other mines, Kirkland Lake, Ontario; Kerr-Addison mine at Larder Lake, Ontario; Morro Velho, Brazil); and at least two have produced more than 20 million ounces (Homestake, S. Dak., and Kolar, India). Homestake is the most productive lode gold mine in the world and has a total production of about 30 million ounces since its discovery in 1876. It is of interest to note, however, that the total output of the Homestake mine is about equal to 1 year's production at present rates from the Witwatersrand district (fossil placer) of South Africa.

The percentage of world gold production attributable to these deposits is difficult to estimate. Most of their production probably has come during the 20th century, although some of them, particularly the California deposits, were mined before 1900, and a few, such as Kolar, India, may have been worked 2,000 years ago or more. These lode deposits have accounted for perhaps 25 percent of the world's gold production since 1900, and in 1969 they yielded 20–25 percent of the world output. They have produced about 25–30 percent of all the gold mined in the United States, and since 1950 they have produced nearly one-half of the U.S. gold output.

Their future importance appears easier to assess. Production from these deposits is fairly steady in the United States, Brazil, and India; is decreasing in

Canada and Australia; and does not appear to be rising appreciably in any country. Although several new mines opened in Canada during the last 10 years, and other new deposits are likely to be found there and elsewhere, the general trend of output is downward.

All the examples cited except Alaska Juneau–Treadwell, Mother Lode–Grass Valley, and Bendigo-Ballarat are in Precambrian rocks, mainly metamorphosed volcanic and sedimentary rocks of the greenstone-granite association, and many of the Siberian lode gold deposits are also in Precambrian rocks. Precambrian terrane appears to be favorable for this type of gold deposit, and it is likely that most new finds will be in areas of Precambrian rocks, such as the Canadian, Brazil-Guyanan, and African-Arabian shields.

EPITHERMAL ("BONANZA") DEPOSITS

Examples of the "bonanza" deposits of the North American Cordillera are Goldfield, Virginia City, and Tonopah, Nev.; Cripple Creek, Telluride, Silverton, and Ouray, Colo.; and El Oro, Pachuca, and Guanajuato, Mexico. Geologically similar deposits occur in Transylvania (Rumania), Nicaragua, the Philippines, New Zealand, and Japan. These deposits are hydrothermal veins of quartz, carbonate minerals, barite, and fluorite containing gold or gold tellurides and variable but commonly large amounts of silver relative to gold. They were emplaced mainly by filling of open spaces, and most of them are in highly altered volcanic rocks of Tertiary age. They were formed within a few thousand feet of the present surface and persist to depths of only a few thousand feet at most, generally much less. The gold content of ore mined is extremely variable; some ore at Goldfield contained 20 ounces of gold per ton, but most ore in these deposits probably contained 0.5–1 ounce of gold per ton, somewhat more than the gold-quartz lodes.

The "bonanza" deposits, although they generally persist only to relatively shallow depths, may contain very large amounts of gold and silver. Cripple Creek, Colo., produced about 19 million ounces of gold, and the Comstock district at Virginia City, Nev., produced 8.5 million ounces, as well as more than 200 million ounces of silver. Other sizable deposits include Goldfield, Nev. (4.2 million oz); Telluride, Colo. (4 million oz plus more than 63 million oz of silver); Tonopah, Nev. (1.9 million oz plus more than 100 million oz of silver); Waihi (4 million oz) and Thames (1.5 million oz) in the Hauraki region, North Island, New Zealand; and El Oro, Mexico (2 million oz).

Gold deposits of this general type probably have been mined for thousands of years, first in Egypt and the Balkans. In the United States their exploitation dates from around 1860, and from then until the 1920's they were a major source of gold. Four deposits alone—Cripple Creek, Virginia City, Goldfield, and Telluride—have produced more than one-tenth of all United States gold, and from 1860 to 1920 they accounted for nearly one-fifth of United States gold production.

Very little gold is produced at present from "bonanza" deposits, and practically none, in the United States. Despite much effort in the United States during the past half century, no new deposit or significant extension of a known deposit has been discovered. Inasmuch as these deposits are probably the most easily discoverable type of bedrock gold deposit, it appears unlikely that they will be a significant factor in future gold production.

YOUNG PLACERS

Examples of young placers are deposits along the American, Feather, and Yuba Rivers in the Sierra Nevada of California; along Alder Gulch at Virginia City, Mont.; on the Yukon River at Fairbanks, Alaska, and on and near the beach at Nome, Alaska; at Klondike in the Yukon Territory of Canada; in the upper Lena, Yenisey, and Amur Rivers in Siberia; and along the east flank of the Andes Mountains in Bolivia, Peru, Ecuador, and Colombia. The Tertiary placers of the Sierra Nevada and the geologically similar placers at Ballarat, Australia, as well as the Upper Cretaceous to lower Tertiary auriferous conglomerates of northwestern Wyoming are also placed in this group; they are older and more consolidated than the typical young placers, but they are more similar to the young than to the fossil placers.

The young placer deposits are composed primarily of unconsolidated or semiconsolidated sand and gravel that contain very small amounts of native gold and other heavy minerals. Most are stream deposits and occur along present stream valleys or on benches or terraces of preexisting streams. Much less commonly, they are beach deposits, as at Nome, Alaska, or are residual deposits, such as those in the saprolite (deeply weathered rock) of the southeastern United States. The deposits contain from a few cents to several dollars worth of gold per cubic yard (1 cu yd of gravel weighs about 1.5 tons, and a very rich placer deposit would thus contain only a few grams of gold per ton of gravel). The largest placers yielded several million ounces of gold; most placers, however, were much smaller.

Placer deposits were easy to find and easy to mine; consequently they were discovered early and were a very important source of gold in the ancient world and indeed as late as the 19th century. Their contribution to total world production cannot be estimated closely, but it probably is between one-fourth and one-third of the total, or somewhere between 750 million and 1 billion ounces.

Since the beginning of gold mining in the United States, placer deposits have yielded about 114 million ounces of gold, or about 36 percent of all gold mined. Of this amount, about 68 million ounces have come from the Sierra Nevada placers of California—about 53–54 million ounces from young placers and 14–15 million ounces from Tertiary placers (Merwin, 1968). Other large U.S. placer deposits include those of Fairbanks, Alaska (7.2 million oz), Nome, Alaska (3.5 million oz), Virginia City, Mont. (2.5 million oz), and Boise Basin, Idaho (2.3 million oz) (Koschmann and Bergendahl, 1968).

Production from placer mines has been declining for many years, and at present the mines yield significant amounts of gold only in the U.S.S.R. and Colombia; they probably account for 5–10 percent of the world production. Placer gold production in the United States in 1969 was only 25,418 ounces, a little more than 1 percent of the total U.S. output. The reasons for this decline are varied—ease of discovery and exploitation and consequent early exhaustion, increasing costs of operations, and, particularly in the United States, environmental problems such as water pollution and siltation.

Placer deposits are not expected to be a significant factor in future U.S. gold production. The country has been so well explored that probably no large deposits remain undiscovered. Moreover, regulations dealing with stream pollution and water use will probably become more stringent rather than less so. Both these factors make it most unlikely that the current downward trend in placer production will be reversed. Worldwide, the situation appears similar to that in the United States. In Colombia, placer production has been significant, but it has been declining gradually and was less than 200,000 ounces in 1969, or only about half the output of 10 years ago. Little is known about production of placer gold from the U.S.S.R. in recent years; perhaps 50 percent of the total production of 290–350 million ounces (estimated) has come from placers, but the percentage derived from these deposits at present is not known. Other formerly productive placers are either virtually exhausted (Egypt, Spain, Australia, Canada) or are being worked on a much reduced scale (Brazil, Peru, Bolivia).

ANCIENT (FOSSIL) PLACERS

Examples of ancient (fossil) placers are the Witwatersrand district, Republic of South Africa; Tarkwa, Ghana; and the Serra de Jacobina, Bahia, Brazil. These deposits are placers that formed in the geologically distant past (all examples are of Precambrian age) and have been lithified to conglomerate to become part of the bedrock; they may thus be termed "fossil placers" in the same sense as the remains of organisms found in rocks are called fossils. These conglomerates consist of small well-rounded pebbles of quartz embedded in a matrix of pyrite and micaceous minerals. In addition, they contain a large suite of heavy and resistant minerals, the most valuable of which are gold, uraninite, and platinum-group metals. The conglomerates were laid down originally on the earth's surface, but they were buried and are now tilted to varying degrees. The individual conglomerate beds generally are only a few feet thick but have lateral extents measured in miles and are known to reach depths of more than 2 miles below the earth's surface. Their gold content ranges from 0.2 to 0.8 ounce per ton; the average grade of gold ore milled in the Witwatersrand district between 1893 and 1969 was about 0.35 ounce per ton (Chamber of Mines of South Africa, 1969, p. 60), at Tarkwa the ore averages 0.2 ounce per ton (De Kun, 1965, p. 91), and at Jacobina the gold content of ore mined is about 0.5 ounce per ton (Gross, 1968, p. 272).

Although the Jacobina deposits were mined as early as the 17th century, this type of deposit did not produce any appreciable part of the world's gold until discovery of the Witwatersrand district in 1886. Since then this great district has become an increasingly important source of gold, and since 1954 it has produced more than one-half of the world's gold output exclusive of the U.S.S.R. It seems safe to say that no other single mining district has dominated the world output of a mineral commodity so completely and for so long as the Rand has dominated gold production; in 1970, for example, 67 percent of the world's newly mined gold came from Rand mines.

The future importance of the fossil placer deposits can hardly be overestimated. The very large reserves—about 600 million ounces according to several recent estimates (Gold Producers Comm., 1967(?), p. 41; Kavanagh, 1968, p. 557; U.S. Bur. Mines, 1972, p. 61)—of the Witwatersrand indicate that the district will continue to be the principal source of the world's gold for many years, even though some dire predictions about the life of the district, based on a fixed price of $35 per ounce for

gold, have been made during the last 5 years (World Mining, 1967). No fossil placer gold district even approaching the size of the Rand has been discovered anywhere in the world, but it seems at least possible that some of the ancient shield areas—Canadian, Brazil-Guyanan, or African-Arabian, in particular—may contain other extensive gold-bearing conglomerates. Indeed, geologically similar uranium-bearing conglomerates were discovered at Blind River (or Elliot Lake), Ontario, Canada, in 1949, but these contain only minor amounts of gold (Roscoe, 1957; Bateman, 1958). No fossil placer deposits have been found in the United States, and extensive fieldwork done in recent years indicates that none are likely to be exposed at the present surface.

MARINE PLACERS

Examples of marine placer deposits that have yielded significant production are lacking. Sediment on the ocean floor in several parts of the world is known to contain small amounts of gold. Most of this gold was derived from the land, transported by streams to the ocean basins, and deposited with clastic sediments on the ocean floor. Some appears to have been derived from the reworking of gold-bearing rocks and sediments on the sea floor. None of these deposits is being mined at present, and the only reported production of gold from a marine placer is a small amount recovered as a byproduct of tin dredging in Malaysia.

The largest known gold-bearing area on the sea floor is in the northern Bering Sea, where concentrations of 30–100 ppb have been found over a very broad area including Norton Sound along the south edge of Seward Peninsula in Alaska (U.S. Geol. Survey, 1968, p. A79; 1969, p. 30). On the continental shelf off Oregon and northern California, concentrations of gold ranging from 10 to 390 ppb have been found in several areas (Moore and Silver, 1968). These deposits are believed to have formed at or near sea level during a lower stand of the sea.

Marine placer deposits of tin are exploited on a large scale in Malaysia, Thailand, and Indonesia, but these placers contain only negligible amounts of gold; a small production of gold is reported from West Malaysia. Beach sand deposits of the titanium minerals ilmenite and rutile in Australia, and similar deposits of ilmenite in Ceylon, also are mined on a large scale, but these apparently contain no recoverable gold.

The future importance of marine gold placers such as those of the Bering Sea is difficult to assess but would appear to be minor. The volume of material available is large, but the gold content is very low, and operating conditions are severe.

DEPOSITS OF DISSEMINATED GOLD

Examples of deposits of gold disseminated in bedrock are Carlin (Hardie, 1966), Cortez (Wells and others, 1969), Getchell (Erickson and others, 1964), and Gold Acres (Wrucke and others, 1968), all in Nevada (Roberts and others, 1971). These appear to be a new major type of gold occurrence, although deposits geologically somewhat similar to them have long been known, such as Mercur, Utah (Butler, and others, 1920, p. 382–395), and Bald Mountain, Deadwood, and others, South Dakota (Irving, 1904, p. 111–162; Connolly and O'Harra, 1929, p. 142–171). All these deposits were brought into production after 1935, and Cortez was discovered in 1966. The deposits consist of very fine grained gold (0.01–10 microns, or 0.00001–0.010 mm) disseminated in silty and carbonaceous dolomitic limestone; at both Carlin and Cortez the host rock is of Silurian age. Gold is accompanied by silica, a little pyrite and other sulfide minerals, and barite. The ore was formed by hydrothermal replacement of the host rock. It contains about 0.3 ounce of gold per ton and very little silver, generally less than 10 percent of the amount of gold, as well as a characteristic suite of trace elements—arsenic, antimony, mercury, and, less commonly, tungsten. Some of the deposits are of Tertiary age, and others may be slightly older; the Carlin deposit has not been dated closely but presumably is within the same age range.

Because only a few deposits of disseminated gold have been discovered, little is known about the amount of gold this type of deposit may contain. Both the Carlin and the Cortez deposits contain more than 1 million ounces of gold, and the Getchell mine has yielded nearly 0.5 million ounces.

These deposits have produced only a tiny fraction of U.S. or world gold; from 1936 to 1969, they yielded slightly more than 2 million ounces, less than 3 percent of U.S. production during that period. However, they have become an increasingly important contributor to United States output, and in 1969 the Carlin and Cortez mines alone accounted for about 22 percent of U.S. production.

The future importance of this type of deposit is difficult to assess on a worldwide basis, but for the United States it is likely to be great. Because of the very fine grained nature of their gold, these deposits went largely unrecognized during the great wave of prospecting in the last half of the 19th century and the early 20th century, and the deposits that were discovered were too low grade to be attractive. The discovery of two major deposits, Carlin and Cortez,

in the 1960's encourages belief in the existence of other unrecognized deposits. The geologic environment of these deposits is still not completely understood but is the subject of much current research; for instance, the geochemical similarity between these deposits and certain modern hot-spring deposits in New Zealand that contain as much as 85 ppm gold and 500 ppm silver has been noted recently by Weissberg (1969). Enough is known, however, to indicate that very large areas underlain by favorable host rocks remain untested; the most likely area for further discoveries is the Antler orogenic belt in central Nevada and its inferred extension in southern Idaho north of the Snake River Plain (Roberts, 1960, 1966).

BYPRODUCT GOLD

Gold is a common minor constituent of base-metal ores and may be recovered when these ores are smelted and refined. Such ores, although data on their gold content are very sparse, appear to contain 0.001–0.025 ounce per ton (0.04–0.9 ppm). Despite the very low gold content, gold production from these deposits is significant because of the large tonnages mined each year. Currently, byproduct gold accounts for 40 percent of the total United States gold output, and 19 of the 25 largest gold-producing mines in the United States yield gold only as a byproduct (Hoyt, 1971, p. 533). Of the byproduct production, 80 percent is from copper ore, and the rest is principally from complex ores of lead, zinc, and copper. Salt Lake County, Utah, which contains the large open-pit copper mine at Bingham, yielded more than half of the byproduct gold produced in the United States in 1969.

Precise figures on the worldwide production of byproduct gold are not available, but this source probably accounts for 5–10 percent of the total world output. Byproduct gold constitutes a significant part—15 percent or more—of the production from several major gold-producing countries, including Australia, Canada, Japan, Nicaragua, Peru, and the Philippines.

In recent years, byproduct gold has been a steady source of supply in the United States, and it is expected to continue to be so into the future. Any change in production will be controlled largely by output of copper and, to a lesser extent, of lead and zinc. Changes in the price of gold will have a negligible effect on production from this source. Similar considerations apply to byproduct gold output in the rest of the world.

RESERVES AND RESOURCES

Many estimates of U.S. and world reserves and resources of gold have been made, and a few are given in table 51. World reserves of gold total about 1 billion ounces, of which 60 percent is in South Africa. At the present rate of production, world reserves would be exhausted in 20–25 years. U.S. gold reserves are 50–80 million ounces, about half of which are in byproduct ores. The remainder are mostly in disseminated and lode deposits.

In addition to reserves of gold in the ground, large amounts are held by governments and banks as official reserves and by speculators and other private holders. Government and bank holdings total 1.3 billion ounces, of which about 292 million ounces was in the U.S. Treasury at the end of 1971. The quantity of gold in the hands of speculators and others, although difficult to estimate, is probably of the order of 1 billion ounces. Clearly, the reserves of gold already mined are considerably larger than those of unmined gold.

The U.S. gold resources shown in table 51 are mostly conditional resources. Hypothetical and

TABLE 51.—*Reserves[1] and potential resources[2] of gold (in millions of ounces) in the world as estimated in several sources of data*

Source of data[3]	A[4]		B	C		D
	Reserves	Potential resources	Reserves	Reserves	Potential resources	Reserves
United States	[5] 9	399	50	[6] 53	[7] 244	82
South Africa	---	---				600
Canada	---	---				25
Australia	---	---	950	300	600	10
Other non-Communist countries	---	---				83
Communist countries (excluding Yugoslavia)	---	---				200
World total	---	---	1,000	353	844	1,000

[1] Reserves: Identified deposits from which minerals can be extracted profitably with existing technology and under present economic conditions.
[2] Potential resources: Identified mineral deposits not profitably recoverable with existing technology and economic conditions, and undiscovered mineral deposits whether of recoverable or subeconomic grade.
[3] A, U.S. Bur. Mines (1967, p. 5); B, U.S. Geol. Survey (1968, p. A13); C, Ageton (1970, p. 577); and D, U.S. Bur. Mines (1972, p. 61).
[4] Exclusive of byproduct gold.
[5] Producible at $35 per ounce.
[6] Producible at 1968 price—about $40 per ounce. Includes 30 million ounces of byproduct gold.
[7] Producible at prices up to $145 per ounce. Includes 30 million ounces of byproduct gold.

speculative resources cannot be estimated as accurately as reserves, but these resources are probably large compared with current U.S. gold production or consumption but small compared with total world reserves. The largest potential resources of gold in the United States are in Tertiary or Cretaceous placer deposits or auriferous conglomerates, followed in decreasing order of magnitude by disseminated, lode, "bonanza," and other placer deposits.

The Tertiary-Cretaceous placer deposits of the United States represent a very large resource of gold, but at the present time they are not economic to mine. The auriferous conglomerates of northwestern Wyoming contain 35–200 ppb gold in a volume exceeding 50 cubic miles, and they probably contain several hundred million ounces of gold (6–10 yr production from the Witwatersrand) (Antweiler and Love, 1967). The Tertiary placers of the Sierra Nevada have an estimated 3–4 billion cubic yards of gravel containing 20–30 million ounces of gold (Merwin, 1968, p. 2). In both areas, formidable and, for the foreseeable future, probably insurmountable technologic and legal problems militate against utilization of these resources.

Deposits of disseminated gold—the so-called Carlin-type deposits—probably contain the second largest domestic resources of gold and almost certainly the largest undiscovered resources of grade high enough to be mined at the present price of gold or even at a substantially higher price. The two largest deposits were discovered as late as the 1960's, and others may well have been missed by earlier prospectors. The area of possible occurrence of favorable host rocks, principally in north-central Nevada, is large, and the known deposits contain enough gold—one-half million ounces or more apiece—to make discovery of others rewarding.

Undiscovered resources of gold undoubtedly remain to be found in the lode- and "bonanza"-type deposits, but the amount is probably small compared with that in the disseminated deposits. The lode and "bonanza" deposits have been sought for many years, and most of them discoverable with present exploration techniques probably have been found. The lode deposits occur principally in rocks of Precambrian age, rocks which have a complex geologic history. Each year our knowledge of the geology of these rocks is improving, and this in time should lead to development of guides that will increase chances for discovery of new deposits. For the "bonanza"-type deposits, a better understanding of the geochemistry of the extensive alteration halo that envelops these deposits might provide a useful tool for recognizing the outer fringes of the halo over a concealed deposit. However, much effort has been expended toward these ends in recent years, but so far no new discoveries have been reported.

Gold resources of young placer deposits must be small; these deposits are easy to find and have been extensively mined, and the likelihood that any young placer of significant size remains undiscovered is very slight. Moreover, the increasingly strict legal restraints on placer mining because of water pollution problems inherent in this kind of mining are discouraging to further prospecting.

Inasmuch as gold may be recoverable even at very low concentrations, materials containing gold in amounts near crustal abundance should perhaps be considered as potential future resources. Such materials would include, for instance, sea floor sediment such as in the Bering Sea, or sea water itself, both of which presumably contain enormous quantities of gold. However, the concentration of gold in both is far too low for economic recoverability at present, and in fact, the average concentration of gold in sea water is so minute as to exclude it from serious consideration as a potential source in the foreseeable future. (At a medium concentration of 0.03 ppb, and with gold at $70 per oz, the gold in a metric ton of sea water would be worth $.0000639; expressed in another way, the amount of sea water that would have to be processed to extract 1 oz of gold, assuming a concentration of 0.03 ppb and complete recovery, would be approximately 1 million m^3—enough water to flood two football fields to a depth of 100 m.)

Not enough is known about uneconomic and undiscovered gold resources outside the United States to permit an estimate of their magnitude at this time. The one figure shown in table 51 (col. C) for gold resources outside the United States represents mainly deposits that are considered reserves by other authorities. It seems clear, however, as noted previously, that the most favorable areas for discovery of new deposits of the two types that historically have been the most productive—the gold-quartz lodes and the fossil placers—are those of Precambrian rocks, particularly rocks in the approximate age range of 1.6–2.7 billion years. Rocks in this age group are hosts for all the major Precambrian gold deposits of the world—Witwatersrand, Homestake, Kolar, Porcupine, Kirkland Lake–Larder Lake, Kalgoorlie, Tarkwa, and probably Morro Velho. Precambrian rocks constitute the Canadian, Brazilian-Guyana, African-Arabian, Australian, and Indian shields and are exposed over extensive areas in Siberia. In the United States, Precambrian rocks older than about 1.6 billion years are not widely

exposed. Their main areas of outcrop are in the eastern ranges of the Rocky Mountains in New Mexico, Colorado, Wyoming, and Montana; in the Black Hills in South Dakota; and in northern Michigan, Wisconsin, and Minnesota around the west end of Lake Superior. Smaller areas are scattered through Arizona, southern Nevada, and southeastern California.

PROSPECTING TECHNIQUES

Because of the nature of gold—its high density, its resistance to tarnish and hence its high visibility, and its distinctive color—the most useful field tool in the search for gold deposits has been the gold pan, with which gold can be recognized immediately if it is in large enough particles. The gold pan is still a useful implement, but it is unreliable for detecting gold tellurides or extremely fine grained gold such as characterizes the Carlin-type deposits. For measurement of unseen gold in rock samples, the fire assay has until recently been the standard method. However, the fire assay is both costly and time consuming and has been supplanted to a large degree by atomic absorption spectrophotometry, a rapid and economical method that can detect as little as 20 ppb gold in a sample. This method has made possible the routine analysis of large numbers of samples and thus has greatly facilitated exploration for gold.

PROBLEMS FOR RESEARCH

Early in 1966, the U.S. Geological Survey undertook a large research program, the Heavy Metals Program, to tackle many of the geologic problems related to gold. This program is no longer in existtence, but research is being continued on many important problems as part of the Geological Survey's mineral-resource program.

A principal geologic problem related to U.S. gold deposits is the geologic and geochemical nature of the disseminated (Carlin-type) deposits. Inasmuch as these deposits probably represent the largest relatively high grade gold resource of the United States, further research on them would appear to have a high possible payoff. Much is already known about the geologic setting and geochemical makeup of these deposits, and they are the subject of continuing research. Nevertheless, no new discoveries have been reported since Cortez, Nev., in 1966. Is some vital clue perhaps being overlooked?

The greatest gold-producing district in the world is the Witwatersrand. Counterparts of the Precambrian gold-uranium placer deposits of the Rand seem to be very rare, and none even remotely comparable in productivity has been found. What critical combination of geologic factors was operative in the formation of these deposits? If this question could be answered satisfactorily, would it be possible to predict where and when other such combinations might have occurred in the geologic past?

Very large amounts of gold must have been eroded from the Precambrian deposits of the Canadian Shield in Ontario and Quebec, yet very little gold has been found in younger rocks overlying the shield along its southern edge even though they were extensively sampled in the Heavy Metals Program. Are there other more likely places where this gold might have been concentrated?

The high concentration of major gold deposits in rocks of intermediate Precambrian age (2,700–1,600 million years) has already been noted. Many of these deposits are in rocks of, or related to, the so-called greenstone-granite association (districts in Ontario and Quebec, Canada; Kalgoorlie, Australia; Kolar, India; Rhodesia). Do the auriferous greenstone-granite terranes have any geochemical peculiarities that would distinguish them from lithologically similar but barren terranes?

Broad alteration halos surround "bonanza"-type gold deposits. Much is being done to characterize these halos chemically and to determine the chemical and mineralogic changes that occur during the formation of a halo and its subsequent weathering. Will it be possible to distinguish a halo associated with an ore deposit from one in barren rock?

Gold deposits occur in mountain ranges at or near enough to the surface to be detected with existing exploration tools. But what of these deposits that undoubtedly occur in adjacent valleys beneath a thick cover of younger sediment? Can exploration tools be developed to detect them? Measurement of the mercury content of air, which is higher over certain types of ore deposits, holds promise. Are there other elements that might be useful?

A group of related problems concerns the distribution of gold in rocks. Considerable information is available on the gold content of various rock types and minerals and of bedrock ores, but many gaps in knowledge remain. For instance, there seem to be three points, or relatively narrow ranges of points, in the spectrum of gold concentrations: (1) crustal abundance of 0.003–0.004 ppm; (2) gold content of the lowest grade gold ore mined in modern times (Alaska Juneau mine, average grade of ore only about 0.04 oz per ton, or a little more than 1 ppm) and of the porphyry copper deposits, which yield gold as a byproduct (0.001–0.018 oz per ton, or 0.04–0.6 ppm); and (3) gold content of ore being

mined at gold mines throughout the world (0.3–0.5 oz per ton, or 10–17 ppm). Is any appreciable percentage of the total gold in the accessible parts of the earth's crust present in concentrations intermediate between those of porphyry copper ore and currently minable gold ore, say 1–5 ppm, or is there a real gap in the concentration range between these two grades of ore, rather than only an apparent one created by mining economics? A corollary question concerns the distribution of gold near deposits of gold and other metals: is gold confined largely to the deposits themselves or does it decrease gradually away from the deposits; that is, does a gold-enriched halo or "assay wall" commonly bound a gold-bearing deposit?

Other gaps in knowledge include the mode of occurrence of gold in minerals, especially those of mafic rocks, and the distribution of gold in porphyry copper deposits and their wallrocks.

A final problem, for the most part not a geologic one, concerns the lack of up-to-date information on the gold resources of the U.S.S.R. Although Russia has the second largest gold production in the world and is believed to have substantial reserves and resources, almost nothing has been published on its production, reserves, resources, or economics since the midthirties. If, as some analysts believe, industrial demand for gold has already reached the current level of production, or will do so in the near future, then Russian output may play an important role in determining both the price of gold and its degree of utilization.

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GRAPHITE

By Paul L. Weis

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ABSTRACT OF CONCLUSIONS

Within the last 20 years technology and attitudes in the graphite industry have changed significantly. In 1950 the domestic industry demanded natural graphite from only a few sources and strongly resisted substitutions. Since 1960, the price of raw graphite has risen because of steadily increasing costs of labor at the source areas abroad and the more recent devaluation of the dollar in the world market. Today, new technology has shown that these old preferences need not be so rigorously applied. Domestic consumption of generally more costly synthetic graphite has increased and by 1969 was seven times that of natural graphite.

This combination of technical and economic factors has generated renewed interest in domestic graphite deposits whose total resources are greater than 10 million tons. Except for one active mine in Texas, no domestic resources of graphite currently seem competitive with foreign sources. Flake graphite deposits in Alabama, New York, and Pennsylvania are probably too low grade to mine now. Flake and amorphous deposits in Alaska are too remote, and vein deposits in Montana are too small to be of commercial value soon.

The likelihood of finding richer, larger, or more favorably located domestic deposits seems slight.

INTRODUCTION

The graphite industry is one of the Nation's smallest mineral industries. The total sales of natural graphite in the domestic industry were less than $6½ million in 1969; however, the unique physical and chemical properties of graphite make it irreplaceable in some uses. The importance of graphite to the national economy is therefore difficult to define precisely, but is far greater than the annual dollar value of commercial sales would appear to indicate.

Graphite is pure crystalline carbon; it is steel gray and has a hardness of 1 to 2, specific gravity of 2.1 to 2.3, and excellent cleavage. It is sectile, flexible, and a good conductor of heat and electricity. Graphite is also extremely inert to most chemical reagents, including hydrofluoric acid and boiling aqua regia. At temperatures above 600°C graphite decomposes slowly in an oxidizing atmosphere, but if protected by a nonoxidizing atmosphere or an inert coating, it remains stable to 3,500°C.

Natural graphite occurs in three geologic environments, and the distinctive qualities of the graphite in each give rise to three categories of commercial deposits.

1. Veins consisting of 75–100 percent graphite are of commercial value, but they are only found in a few places where they cut igneous and metamorphic rocks, commonly of Precambrian age. The graphite is marketed as "lump and chip," "crystalline lump," or "amorphous lump," in various classes depending on particle size and purity.
2. "Flake graphite" is the commercial designation for graphite that occurs as flakes disseminated through layers of metamorphosed carbonaceous sedimentary rocks. Commercial deposits contain from about 8 to more than 20 percent graphite. The thickness, toughness, density, size, and shape of the flakes vary by the deposit.
3. "Amorphous graphite" is a commercial designation for any massive, very fine grained graphite, most of which comes from thermally metamorphosed beds of coal. Deposits of commercial value generally contain at least 80 percent graphite.

Industrial uses of graphite depend upon the characteristics of the three natural graphite types. Fine-grained, relatively low cost "amorphous" graphite is used extensively for foundry facings, certain refractories, and as a source of carbon in steelmaking. Flake graphite is prized for high-quality lubricants and for high-quality crucibles and refractory ware. "Amorphous lump," or vein graphite, is also used in lubricants and refractory ware but is especially desired for carbon brushes in electric motors. The uses of the graphite consumed in the United States in 1969 are summarized in table 52.

The industrial importance of the three types of natural graphite is reflected in the tonnage of U.S. imports shown in table 53. Amorphous graphite, chiefly from Mexico, has averaged about 80–85 percent of total imports. Shipments from Madagascar and Ceylon in recent years have been on the order of 4,500 and 2,500 tons, respectively. Although the proportion of Ceylon graphite classified as crystalline lump and lump and chip (vein type) is not clear, it probably amounts to less than 50 tons per year in recent years.

The only domestic graphite mine now active, that at Burnet, Tex., produces flake graphite. Deposits of similar material, however, occur in many other places in the United States, chiefly in Alabama, Alaska, New York, Pennsylvania, and other places in Texas. Deposits of vein graphite occur in Montana and New York, and deposits of amorphous graphite occur in Rhode Island, New Mexico, and Colorado. The unproductive deposits are not economically competitive with foreign sources of natural graphite.

Natural graphite now faces competition from synthetic graphite, marketed as "artificial graphite." The commercial name is a misnomer insofar as it implies an imitation, because the product is really crystalline graphite produced in high-temperature furnaces from petroleum coke or other forms of amorphous carbon. Synthetic graphite is a product of high purity, but it tends to be finer grained, less dense, and more expensive than most natural flake graphite. Synthetic graphite can be substituted to some degree in all of the uses of natural graphite,

TABLE 52.—*Consumption, by uses, of natural graphite in the United States in 1969*

Use	Short tons	Value (thousands)
Batteries	(1)	(1)
Bearings	104	$51,307
Brake linings	1,066	368,998
Carbon brushes	588	285,869
Crucibles, retorts, stoppers, sleeves, and nozzles	4,639	780,793
Foundry facings	8,028	1,017,221
Lubricants	2,702	492,316
Packings	409	182,983
Paints and polishes	182	27,997
Pencils	2,190	666,095
Refractories	5,554	735,419
Rubber	225	73,054
Steelmaking	6,624	578,386
Other [2]	4,853	1,093,359
Total	37,164	6,353,797

[1] Withheld to avoid disclosing individual company confidential data; included in "Other."

[2] Includes adhesives, chemical equipment and processes, electronic products, gray iron castings, powdered-metal parts, small packages, specialties, and batteries. Data from U.S. Bur. Mines.

TABLE 53.—*Tonnage and value of 1969 U.S. imports for consumption of natural graphite, by countries*

[Data from U.S. Bureau of Mines]

Country	Total	
	Short tons	Value (thousands)
Austria	20	$2
Ceylon	3,517	402
France	16	9
Germany, West	1,535	246
Hong Kong	337	8
Italy	18	8
Korea, South	618	17
Malagasy Republic	5,042	507
Mexico	43,269	876
Norway	4,037	334
Sweden	44	4
Switzerland	6	2
United Kingdom	20	4
Total	58,479	2,419

though its higher cost makes it noncompetitive for some uses. Synthetic graphite, however, is the only product that is pure enough for use in moderator rods in nuclear reactors. It is also used in electrodes for electrosmelting and in anodes for the electrochemical industry. Total consumption of synthetic graphite in the United States has increased steadily over the last 20 years and in 1969 was 225,500 tons, almost seven times the total tonnage of natural graphite consumed. The use of synthetic graphite in future industrial markets undoubtedly will affect the mining of natural graphite.

Other details of the economic aspects of the graphite industry are given by Lewis (1970).

EXPLOITATION

Graphite production in the United States began between 1644 and 1648 at Sturbridge, Mass., but between that time and about 1850, production, which came from scattered operations in New England, New York, and New Jersey, apparently was small and sporadic. During the period 1850–1900, deposits in New York, New Jersey, Alabama, Pennsylvania, Michigan, Texas, California, Nevada, and Rhode Island were explored and developed, and a domestic graphite industry came into being. From the 1850's to 1900, the mines of the Joseph Dixon Co. near Ticonderoga and Lake George, N.Y., were the principal domestic source of flake graphite, but around 1900, Alabama and eastern Pennsylvania began intermittent production of substantial amounts of flake graphite. In 1911, Alabama took first place as a producer of flake graphite and maintained that position until after World War II. From about 1946 to 1954, Texas and Alabama produced nearly equal amounts of flake graphite. By the end of 1954, all flake graphite production had stopped. After a short lapse, production in Texas resumed in 1955 and has continued to the present at the Southwest Graphite Co. mine in Burnet County.

Amorphous graphite was apparently first mined in quantity from deposits in Rhode Island, North Carolina, California, and Nevada, then later in Michigan, Wisconsin, and other States. By the end of 1954, only one deposit of amorphous graphite in Rhode Island was being mined. Tonnage and quality of the deposits in these States are both lower than the Mexican sources that have supplied a large part of our needs since World War I.

A high proportion of the annual consumption of natural graphite in the United States is by the ferrous and nonferrous metals industries where it is used for foundry facings, carburizing, and a wide variety of refractory ware. Total consumption and, to a lesser degree, total imports therefore, approximately reflect the general level of prosperity and industrial productivity in the United States (fig. 31).

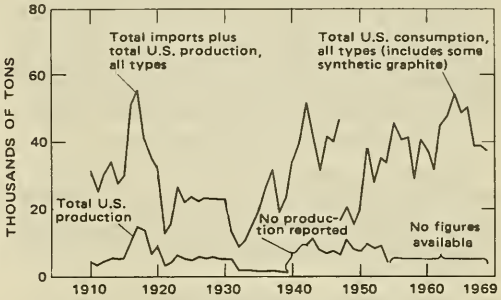

FIGURE 31.—U.S. consumption of graphite, 1910–69.

Industrial activity during World War I caused graphite production and imports to reach a record high; the great depression of the 1930's caused them to reach a record low. World War II, the postwar boom of the 1950's, and the Korean and Viet Nam Wars also caused peaks in graphite consumption. The general recession of 1949, intensified by disastrous strikes in the coal and steel industries, marks the deepest low since the early 1930's.

The data shown in figure 31 also reflect one of the major problems of the prospective U.S. producer—that of fluctuation of graphite consumption. Since 1949, U.S. annual consumption has ranged from 15,000 to 52,000 tons, a difference of more than 340 percent. Only with bravery and optimism can capital and effort be invested in a business that fluctuates so widely and unpredictably.

Until recently there has been strong resistance by industry to graphite from any but long-established foreign sources, notably the Malagasy Republic for flake, Ceylon for both flake and vein, and Mexico and Korea for amorphous graphite. Several reasons account for the favored position that foreign graphite commanded. Supplier's formulas for refractory ware were based on trial and error. Certain graphite plus certain clay plus certain mixing and annealing gave products with a long life. Changes in ingredients or preparation methods shortened the life of the product, thus changes in formulas were strongly resisted. Uses of lubricating flake demanded coarse- rather than fine-grained material, a preference favoring Malagasy flake over others. Finally, many overseas suppliers had been in business long enough to have demonstrated their ability to maintain quality and provide reliable delivery at prices well below

that of most domestic producers. Since about 1960, however, technological changes and increased prices for raw graphite have changed the attitudes of importers and suppliers. Development of the silicon carbide-graphite crucible, which can use graphite from almost any source, is an example of improved technology. The net result is that domestic deposits, particularly those of flake graphite, look much more attractive now than they did in the 1950's or 1960's.

GEOLOGIC ENVIRONMENT

The form, occurrence, mineralogy, origin, and distribution of natural graphite have been discussed in considerable detail elsewhere (Cameron and Weis, 1960, p. 206–208; 241–249) and will be described only briefly here.

GEOCHEMISTRY

Carbon is 11th in abundance among the elements that form the earth's crust, but the crustal abundance of carbon bears little relationship to the abundance or distribution of graphite. Most of the carbon in the crust of the earth—probably 80–90 percent—is in carbonate rocks, and most of the remaining carbon occurs in living or fossil organic matter or in the atmosphere as CO_2; probably less than one-half of 1 percent of the carbon in the earth's crust occurs in elemental form, as amorphous carbon, graphite, or diamond.

Carbon's behavior in the geochemical cycle depends largely on its form. More than 95 percent of the earth's carbon occurs as CO_2 or its compounds, and most of the remainder occurs as one of the hundreds of organic hydrocarbons. These compounds have characteristic geochemical cycles that are unlike that of elemental carbon.

Carbon that occurs as graphite came at least in part from organic material. Once in the form of graphite, it is likely to remain unchanged. In most chemical environments, graphite is one of the most inert substances known to man. Acids, bases, oxidizing and reducing environments alike leave it unchanged. Only at temperatures greater than about 600°C in an oxidizing environment does it slowly change to CO_2. Under surface weathering conditions it remains unchanged. Metamorphism tends to recrystallize graphite to coarser grains. The graphite cycle tends to become a closed system once the mineral is formed.

The cycle of erosion, transportation, deposition, and metamorphism tends to disseminate graphite, rather than to concentrate it. There are no workable sedimentary deposits of graphite. Economic deposits of flake or amorphous graphite occur only where concentrations of nongraphitic carbon have been metamorphosed.

GEOLOGY

VEIN GRAPHITE

Vein deposits of graphite are fracture fillings that contain 75–100 percent graphitic carbon. Crustification is common, with coarse, platy, or needlelike interlocking crystals apparently grown inward from both walls. Mineral impurities include quartz, feldspar, pyrite, pyroxene, apatite, and calcite. Veins range from thin films to massive bodies more than 10 feet in thickness. Some extend along strike for thousands of feet, and some have been mined downdip for more than 1,500 feet. The veins cut both igneous and metamorphic rocks, generally of Precambrian age.

Vein graphite deposits are known near Crown Point, N.Y., and in the Dillon area, Montana, but the only economically important world supply is from Ceylon.

The agents of transport and precipitation of carbon that lead to the formation of graphite veins are not understood. Some geologists have suggested that the veins are hydrothermal; others, that they are pneumatolytic. Neither the hydrothermal nor the pneumatolytic hypothesis has enough supporting field evidence to enable one to make a final choice.

FLAKE GRAPHITE

Flake graphite of commercial size is derived from carbonaceous material in sedimentary rocks that have metamorphosed at least to garnet grade. The resulting gneisses and schists are the hosts for all deposits of flake graphite. The grade of the deposit is dependent on the carbon content of the original sedimentary rocks. Graphitic metasedimentary rocks contain from a trace to as much as 90 percent flake graphite, but most of these gneisses and schists contain less than 3 percent graphitic carbon. Distribution of the graphite in flakes, that may range from 1 to more than 250 millimeters in diameter, generally is more uniform along strike and dip than from one layer to another.

Impurities in flake graphite are the common minerals of high-grade metasedimentary rocks, especially quartz, feldspars, mica, amphibole, and garnet. The suite of gangue minerals is an important economic consideration. Most of these minerals are easily separated from the graphite. Mica is a notable exception, especially when intergrown with graphite, a common relation in many flake deposits. The separation of these minerals becomes extremely

difficult if fine grinding is necessary because the mica becomes coated with a film of graphite and is collected along with the graphite, and the grade of the graphite concentrate is thereby lowered. Marketable concentrates generally contain 85 percent or more graphite.

Probably the largest deposits of flake graphite in the United States occur in gneiss and schist in the Kigluaik Range on the Seward Peninsula, Alaska. The graphitic rocks are exposed for 60 miles along strike, and many layers containing about 10 percent graphite are more than 25 feet thick. Within these layers are lenses and pods containing 50–60 percent graphite, part of which is coarse flake. Most of these lenses and pods are ½–1½ feet thick and 10–20 feet long, but some are as much as 6 feet thick and 100 feet long. Within parts of the range, in the zone of graphitic schist, these high-grade pods are estimated to make up 25 percent of the rock (Coats, 1944).

Deposits of flake graphite in the United States have been mined in Alabama, Alaska, New York, Pennsylvania, and Texas.

The world's most economically important flake deposits now in production are in Malagasy Republic, where layers 10–100 feet thick contain 10–20 percent graphite. Much of the ore is intensely weathered and requires only a simple wash to produce a concentrate containing 85–92 percent graphite. Other important foreign deposits of flake graphite are in Austria, Norway, Russia, and China.

AMORPHOUS GRAPHITE

Amorphous graphite, formed by thermal metamorphism of coal beds, is massive and cryptocrystalline. The size, grade, and mineral impurities in the deposit depend on the characteristics of the original coal seam. Major deposits being mined today generally contain at least 85 percent graphitic carbon. The material is dried, shipped, and used without beneficiation. Operations are successful only if large quantities of material of reliable quality can be supplied at low cost. The most important single factor in marketing amorphous graphite today is transportation cost.

In the United States, small amorphous graphite deposits are known in Rhode Island, near Raton, N. Mex., and near Chaffee, Colo. Major free-world sources are Sonora, Mexico, and Korea.

RESOURCES

The graphite resources of the world are undoubtedly great, but their extent is unknown. Reserves are known for a number of operating mines, but reasonable estimates of potential resources probably are not available for a single major graphite district in the world. The principal reason is that graphite is a relatively abundant and widespread mineral, and known deposits in many areas far exceed current or foreseeable demands, making it understandably difficult to generate interest in making careful resource estimates. As of 1972, deposits containing a total of many hundreds of millions of tons are known, and total world resources may be many times that amount.

IDENTIFIED AND HYPOTHETICAL RESOURCES

The identified resources of graphite in the United States as of 1960 are summarized in table 54. So little prospecting and mining has been done since 1960 that these estimates of recoverable graphite have not yet been improved.

TABLE 54.—*Identified resources of graphite of the United States* [1]

[Summarized from Cameron and Weis (1960, p. 252)]

District	Type of deposit	Recoverable graphite (tons)
Dillon, Mont	Vein	<5,000
Alaska	Flake, vein(?)	>10,000,000
Alabama	Flake	>300,000
New York	---do	>250,000
Pennsylvania	---do	>10,000
Southwest Texas	---do	50,000 ±

[1] Identified resources are specific, identified mineral deposits that may or may not be evaluated as to extent and grade, and whose contained minerals may or may not be profitably recoverable with existing technology and economic conditions.

Most of the graphitic rocks of Alabama, New York, and Pennsylvania contain less than 5 percent graphite, although a few contain as much as 10 percent. The location and ease of mining these deposits suggest that a modest increase in the price of raw graphite might herald the start or resumption of commercial production in these States, especially Alabama. The largest domestic graphite deposits occur in the gneiss and schist in the Kigluaik Range of the Seward Peninsula, Alaska (Coats, 1944). These deposits are higher grade than those in the eastern United States, but the greater distance from markets and the greater difficulty of mining them will retard their commercial development.

The world's identified and hypothetical resources of graphite are summarized in table 55.

The best known provinces of vein graphite deposits are in Montana and Ceylon where the veins cut Precambrian gneiss and igneous rocks. Further search in these areas may reveal additional deposits. The graphitic metamorphic rocks of the Kigluaik Range, Alaska, have been intruded by igneous rocks,

TABLE 55.—*Identified*[1] *and hypothetical*[2] *graphite resources of the world*

Locality	Quantity
Rock containing at least 4 percent graphitic carbon as flake graphite	
North America:	
Canada	>1 million tons.
United States	Millions of tons.
South America:	
Argentina	A million tons(?)
Brazil	Millions of tons.
Europe:	
Austria	Hundreds of thousands of tons.
Finland	Less than 1 million tons.
France	Do.
West Germany	Several million tons.
Italy	A few hundred thousand tons.
Norway	Do.
Spain	Do.
Sweden	Tens of millions of tons.
Asia:	
U.S.S.R.	Hundreds of millions of tons.
Ceylon	Hundreds of thousands of tons.
China	Probably at least millions of tons.
India	Hundreds of thousands of tons.
Japan	A million tons(?)
Korea	Many millions of tons.
Turkey	Tens of thousands of tons(?)
Africa:	
Kenya	Hundreds of thousands of tons.
Malagasy Republic	Many hundreds of millions of tons, in many districts, in an area 100 by 600 miles.
Tanzania	Hundreds of thousands of tons(?)
Uganda	Small.
Zambia	Possibly millions of tons.
Australia:	
South Australia	Possibly millions of tons.
Amorphous graphite in deposits containing about 85 percent graphitic carbon	
North America:	
Canada	Considerable graphite in eastern Canada is too fine grained to be marketed as flake. Total reserves may be several million tons, mostly low grade.
Mexico	Hundreds of millions of tons, containing 80–85 percent graphite.
United States	A few thousand tons of 80–85 percent graphite. Byproduct fine material from flake graphite deposits—possibly several thousands of tons.
	Alaska—byproduct, millions of tons that would require upgrading.
Europe:	
Austria	Hundreds of millions of tons.
Czechoslovakia	Millions of tons.
West Germany	Hundreds of thousands of tons.
Sweden	Two hundred million tons.
Asia:	
U.S.S.R.	Tens of millions of tons. Good quality.
China	Probably many millions of tons, possibly many tens of millions of tons.
Hong Kong	Thousands or tens of thousands of tons.
India	Possibly thousands of tons.
Japan	Tens of thousands of tons.
Korea	Hundreds of millions of tons.
Africa:	
Morocco	A few million tons.
Southwest Africa	Thousands of tons(?)
Australia:	
Queensland	Millions of tons.
Vein graphite in veins consisting of at least 90 percent graphite	
United States	Less than 10,000 tons.
Brazil	Occurrences are reported. Details are unavailable.
U.S.S.R.	Large deposits are reported west of Irkutsk, in eastern Siberia.
Ceylon	The major world supply of vein-type graphite is believed to be here. Total reserves are only estimates from millions of tons to possibly tens or hundreds of millions of tons.
China	Vein-type deposits are reported. Reserves may range from thousands to millions of tons.

[1] Specific, identified mineral deposits that may or may not be evaluated as to extent and grade, and whose contained minerals may or may not be profitably recoverable with existing technology and economic conditions.

[2] Undiscovered mineral deposits, whether of recoverable or subeconomic grade, that are geologically predictable as existing in known districts.

and this area should be explored for possible deposits of vein graphite. Few details are known about the veins of graphite reported in China, the U.S.S.R., and Brazil, and their commercial potential is still mostly unevaluated.

SPECULATIVE RESOURCES

The geology of the Eastern United States is so well known that the likelihood of finding new deposits of flake graphite closer to market is very small. Igneous activity in the coal fields of the United States either did not occur or was of a scale small enough to preclude the chances of finding amorphous graphite deposits of commercial size and grade. Certainly none found are likely to rival the size and grade of the great deposits of Sonora, Mexico.

PROSPECTING

The simplest and most effective means of finding graphite is to look for it in outcrops and residual soil. Because of its chemical inertness, graphite remains completely unaltered in weathered material; and the dark, lustrous flakes are conspicuous in surface soil.

As in prospecting for any mineral, a knowledge of areal geology of the area is the first step in prospecting for graphite. Flake graphite occurs only in metamorphic rocks—commercial sizes generally in schists and gneisses of garnet grade or higher or in marbles associated with other metasediments. Amorphous graphite forms only by thermal metamorphism of coal; therefore, areas to prospect are those where coal-bearing sediments may have been intruded by igneous rock. Vein graphite is so rare and its origin is so poorly understood that it is difficult to characterize the most favorable places to prospect. Most known graphite veins cut Precambrian igneous and metamorphic rocks, although a few are known to be in younger metamorphic rocks as well.

PROBLEMS FOR RESEARCH

Little effort with modern tools has gone into the geologic study of graphite deposits in the United States recently, chiefly because most of the known deposits were considered noncommercial, reasonably priced graphite has been available continuously from foreign sources, and synthetic graphite has acquired a large share of the market. Better techniques to beneficiate the low-grade ores are needed if a domestic industry is to be viable. Studies on the nature of formation of graphite veins might aid considerably the science of ore deposits as well as the search for more graphite deposits. The role of organic matter in metamorphism and hydrothermal ore deposits is not well understood.

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HELIUM

By Dwight E. Ward and Arthur P. Pierce

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ABSTRACT OF CONCLUSIONS

Helium, because of its light weight, chemical inertness, and very low temperature in liquid form, is important in space exploration, industry, and research. It is recovered as a by-product from natural gas used for fuel and has not been a target for independent exploration.

This situation will change, however, when the few large gas fields that now supply most of the helium are exhausted, unless comparable deposits are found. Natural gases with little or no fuel value but appreciable amounts of helium occur in various places in the Rocky Mountain region, but their potential for supplying helium needs of the future is unknown.

Inasmuch as helium originates from uranium and thorium derived from igneous rocks, accumulations are not necessarily limited to areas where oil and gas are found. Uranium-mining areas and volcanic and geothermal areas of the Western United States have untested potential for helium accumulation.

Billions of cubic feet of helium are being wasted annually in the production of natural gas from which the helium is not removed. Better and cheaper methods of helium recovery are needed to save this helium for the future.

INTRODUCTION

Helium, a lightweight, inert gas, is an end product of the radioactive decay of uranium and thorium in rocks. In World War I, the first attempts were made to obtain helium from natural gas for use in lighter-than-air craft, but it was not until World War II that this use was realized on a large scale. The abundant and dependable supply developed during World War II has made helium available for various uses that now overshadow military needs. The properties of lightness and inertness have made helium useful in the space exploration program, the largest user. Either or both of these properties have made helium useful in creating controlled atmospheres for welding certain metals and for growing crystals, for various other industrial processes, for use in chromatography, for heat transfer in nuclear reactors, for leak detection, for breathing mixtures, and for various laboratory researches. In cryogenics research and engineering, liquid helium is used to obtain temperatures near absolute zero.

Assuming that helium will continue to be available in large volumes at reasonable cost, all the previously mentioned uses are expected to increase in the future, and new uses will probably appear. One potential use is as a coolant in power transmission, where conductors at the temperature of liquid helium become superconductors, thereby increasing the efficiency of power transmission lines. In power generation by nuclear fusion, envisioned for the future, thermonuclear reactions may be confined by magnetic fields produced by high-intensity superconducting magnets which will use liquid helium for a refrigerant. The nuclear power industry could become a limited source of helium from the disintegration of nuclear fuels.

The United States, because of its early development of natural-gas resources for fuel, was the first country to find large resources of helium, which is present in natural gas in trace to small amounts, along with other nonflammable gases such as nitrogen, carbon dioxide, and argon. When the natural gas is liquefied, the helium remains a gas and is recovered as crude helium for further refinement. Much of the growth in the use of helium in the United States was due to its availability at reasonable prices from the huge natural-gas fields of the Texas and Oklahoma Panhandles and southwestern Kansas.

From 1950 to 1968, annual use of helium in the United States increased more than tenfold, from 81 to 842 million cubic feet (fig. 32) (Lipper, 1965, p. 437; 1970, p. 84). In 1968, in addition to the 842 million cubic feet of helium sold in the United States, about 25 million cubic feet was exported, and 3,988 million cubic feet was pumped into underground storage as part of the government's long-range conservation program (Lipper, 1970, p. 84). Helium not separated from natural gas when the gas is withdrawn for fuel is lost to the atmosphere. Helium pumped underground and stored will assure a future supply, possibly for several decades after the natural gas has been exhausted.

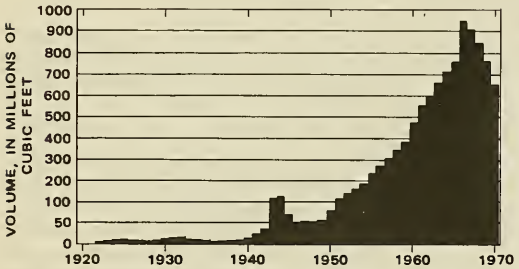

FIGURE 32.—Helium sales in the United States, 1920–70. Adapted from Seibel (1968, fig. 8).

In 1968, use of helium outside the United States was probably not more than 100–150 million cubic feet. Canada supplied about 3 percent of the free-world supply from one recovery plant in Saskatchewan (Lipper, 1970, p. 79). In 1969, France began recovering helium from natural gas supplied by the Netherlands, and the U.S.S.R. produced 70 million cubic feet of helium.

The United States has the largest known reserves of helium, which, at the present level and rate of use, are expected to supply the Nation's needs until at least the end of this century. Intensive exploration for and development of natural-gas resources, which have begun outside the United States only within the last decade or two, doubtless will lead to discovery of new helium resources as well.

GEOLOGIC ENVIRONMENT

Although helium is of great cosmic abundance, second only to hydrogen, it is one of the rarer elements of the earth. Uranium and thorium are radioactive elements that are present in trace amounts in all rocks, but they are most abundant in the accessory and iron-rich varietal minerals of granitic igneous rocks and in dark shaly marine sedimentary rocks (Clark, 1966, p. 522–540). During the radioactive decay sequences in which these elements are transformed to lead, each alpha particle given off becomes a stable helium atom (Rutherford and Royds, 1909):

$$U^{238} \text{ ------} 8He^4 + Pb^{206}$$
$$U^{235} \text{ ------} 7He^4 + Pb^{207}$$
$$Th^{232} \text{ -----} 6He^4 + Pb^{208}$$

Almost all the helium atoms in natural gas are of the heavier He^4 isotope (atomic weight, 4); the lighter He^3 isotope (atomic weight, 3) occurs only in trace amounts and is thought to originate from tritium, the radioactive isotope of hydrogen (Aldrich and Nier, 1948). He^3 is about 10 times more abundant in helium in the atmosphere than in helium in natural gas and is produced by various actions of cosmic rays and by auroral precipitation of solar wind plasma (Johnson and Axford, 1969, p. 2436). Helium atoms, because of their low atomic weights, are able to escape from the earth's atmosphere to outer space, and as a result their average concentration in the atmosphere is only 4 or 5 parts per million.

Studies of the amounts of radiogenic helium in minerals, natural gas, and the atmosphere suggest that less than half the helium formed in rocks is retained in the mineral structures; the remainder is either dissolved in interstitial fluids, entrapped with other natural gases as a gaseous phase in rocks, or lost to the atmosphere (Hurley, 1954; Damon and Kulp, 1958).

The helium that is distributed in sedimentary rocks probably migrates through porous aquifers either as a gas or in the connate waters, or it travels along fractures. Some of it may have leaked into sedimentary rocks from deep crystalline rocks that underlie the sedimentary strata. Much of it is probably first dissolved as a trace constituent in connate waters from which it was expelled as the water

moved upward into traps in the sedimentary column. Concentrations of helium found by drilling occur mixed with other kinds of natural gas, particularly the hydrocarbon gases, nitrogen, and carbon dioxide. Helium in concentrations higher than that of the atmosphere has also been found in the firedamp of many coal mines, in gases from mineral springs, in volcanic gases, and in gases from glacial till and other shallow sources.

Many natural-gas fields have been tested for helium by the U.S. Bureau of Mines (Anderson and Hinson, 1951; Boone, 1958; Munnerlyn and Miller, 1963; Miller and Norrell, 1964a, 1964b, 1965; Moore, Miller, and Shrewsbury, 1966; Moore and Shrewsbury, 1966, 1967, 1968; Cardwell and Benton, 1970a, 1970b, 1971). The analyses indicate that in general the concentration of helium in gas fields increases with geologic age of the reservoir rocks (Pierce, 1960). Gas with more than 0.3 percent helium occurs mostly in geologically old rocks, generally of Paleozoic age, and less extensively in younger rocks.

Dobbin (1968) briefly described the occurrences of helium and other nonflammable natural gases that have been found in the United States and Canada, and Jodry and Henneman (1968) reported on the occurrence, origin, and other aspects of helium.

RESOURCES

IDENTIFIED AND HYPOTHETICAL RESOURCES

All helium recovered in the United States except that from gas fields in the Shiprock area of northwestern New Mexico (discontinued in 1969) and from the Pinta Dome field near Navajo, Ariz., has come from Kansas and the panhandle areas of Oklahoma and Texas. Recovery has been from gases with helium content of 0.3 percent or more, the minimum content considered economically feasible to recover with present technology (Lipper, 1970, p. 82).

So long as natural gas continues to be produced in quantity, helium-rich gas fields will continue to be the main source of helium as a byproduct. According to U.S. Bureau of Mines estimates (Thomasson, 1971, p. 4), at the end of 1970 at least 80 percent of proved helium reserves of 154 billion cubic feet in gases containing 0.3 percent or more of helium were in the five fields—Hugoton, Panhandle, Greenwood, Keyes, and Cliffside (table 56)—that now produce most of the helium. The remaining proved reserves are in 83 scattered fields in Arizona, Colorado, Kansas, Montana, New Mexico, Oklahoma, Texas, Utah, Wyoming, and West Virginia. In most of these fields the helium is not recovered as the gas is withdrawn for fuel.

The reserves of natural gas of the United States and Canada are reported annually by the American Gas Association and the Canadian Petroleum Association, respectively. The Potential Gas Agency publishes biennial estimates of the potential gas supply that is as yet undiscovered. Using the 1968 figures of these organizations for average helium content of gases in the various regions, Lipper (1970, p. 82) estimated total helium resources of the United States at about 935 billion cubic feet. He divided this figure into 250 billion cubic feet of proved reserves, 155 billion probable, 220 billion possible, and 310 billion speculative. The average helium content on which these figures are based ranges from 0.006 percent in the gulf coast of Louisiana and Texas, where gas reserves and potential are large, to 0.278 percent in a seven-State area extending from Minnesota and Michigan southward to Missouri, where natural-gas reserves and potential are small.

The extent of helium resources outside North America is mostly unknown because the natural gas resources are not well known. Significant discoveries have been reported in Canada, Africa, the Middle East, and the U.S.S.R.; however, commercial production from these countries is small. On the basis of a geologic comparison of the sedimentary rocks of the world with those of the United States, Hendricks (1965) estimated the possible ultimate discoveries of natural-gas resources of the sedimentary basins of land areas and their bordering continental shelves. Assuming that these gas resources contain amounts of helium comparable to those of the United States, on a volume-for-volume basis, an estimate of possible ultimate discoveries of helium outside the United States is nearly seven times that of the United States, which is estimated to have more than 1 trillion cubic feet. The estimate for the United States, however, includes the Hugoton, Panhandle, and adjacent gas fields with huge gas volume and large helium content. Gas fields of comparable size occur elsewhere, but thus far none have been reported with comparable helium content. Therefore, such an estimate of world helium resources, at this stage, is highly optimistic.

How much of the discoverable resources of natural gas and helium might be economically recoverable depends on economic, geological, and geographical factors, which, for the present, are mostly unknown. For example, liquefied natural gas (LNG) is now becoming an important export from countries with large gas resources. The liquefaction process leaves a residual gas enriched in helium. This helium can be recovered and sold if there is sufficient market demand.

SPECULATIVE RESOURCES

Helium, although now supplied as a byproduct of natural-gas fuel, originates from different source materials and therefore is not necessarily limited to oil and gas areas. Because of the extensive exploration for natural gas for fuel and because helium needs are being satisfied from known gas fields, a separate search for helium has not been necessary. When the few large gas fields that now supply most of the country's helium needs are exhausted, helium may cease to be a byproduct of natural gas and may become a target for direct exploration. If this happens, then some of the gas deposits in Paleozoic rocks in the Rocky Mountain region that have such high content of nitrogen or carbon dioxide as to be unsatisfactory for fuel may become economically valuable for their helium content. The extent of these gas deposits is not known because most developers do not explore beyond the original discovery well. Three such deposits, the Woodside and Harley Domes of Utah and the Model Dome of Colorado, have been set aside as helium reserves. A fourth deposit of this type, the Tip Top field occurs in western Wyoming. Only the Pinta Dome field in Arizona is producing gas solely for its helium content. The remaining gas in the field is mostly nitrogen.

Regions within which deposits of nonfuel gases are known cover at least 20,000 square miles. Lipper (1970, p. 83) reported that about 8 percent of the known domestic helium reserves (in gases containing more than 0.3 percent helium) is in gases that are noncombustible or that have such low heating value that they are not salable as fuel. The extent of these nonfuel gases is unexplored in large areas.

Sedimentary rocks derived from the erosion of igneous rocks may be sources of helium because of the uranium and thorium content of the sediments. (See chapter on "Nuclear fuels.") Helium atoms, because of their very small size and light weight, are able to migrate through very small pore spaces and fractures to reach traps where other natural gases accumulate.

The minute amounts of uranium and thorium present in rocks and the long time required for their radioactive decay indicate that time is an important factor in the accumulation of helium deposits. Hydrocarbon gases form comparatively quickly, and the greatest volumes have been found in Tertiary and Cretaceous rocks. Helium concentrations, on the other hand, are largest in the Paleozoic rocks. Some of the gas fields of the United States and Canada which contain comparatively high percentages of helium are listed in table 56.

The information in table 56 suggests the following potential source rocks and localities, both within and outside oil and gas areas, in which future exploration for helium may hold promise.

1. Black shales and other dark-colored sedimentary rocks having comparatively high radioactivity and of large extent and volume could generate helium that would be trapped in overlying rocks, particularly in rocks of Paleozoic age. Examples of such possible source rocks are the Pennsylvanian Heebner Shale Member of the Oread Limestone in shales of the Pennsylvanian Cherokee Group in Kansas and equivalents in Oklahoma and the Devonian and Mississippian Chattanooga Shale and equivalents of the midcontinent region. Gamma-ray logs of these rocks reveal high radioactivity.
2. Granitic rocks of basement highs and "granite wash" derived from these highs are the probable sources of helium in the Panhandle and Otis-Albert gas fields (table 56). Little natural gas has been found north and northeast of the Central Kansas uplift, but study of the basement rock map of the United States (Bayley and Muehlberger, 1968) suggests that this would be a good area in which to look for gas with appreciable helium content. Although gas deposits in this area apparently would not be large and the gases from them might have little or no value as fuel, they would be found at comparatively shallow depths.
3. Igneous rocks apparently are the source of helium in the gas fields of New Mexico and Arizona listed in table 56. This apparent source suggests that other areas of igneous activity, which were very extensive in the Western United States, may also have helium resources both in natural gas deposits and in geothermal areas. In many areas, exploration and development of geothermal sources of energy are receiving much attention, and in some of the areas the fluids and gases may be abnormally high in helium.

Most of the gas fields listed in table 56 are on or near the highest parts of uplifts. The largest accumulations of helium in the United States are in structurally high areas around the southern, western, and northern margins of the Anadarko basin of Oklahoma. Natural-gas fields occur also in structurally lower parts of the basin, but these do not contain large amounts of helium. Contours of the basement surface on the basement rock map of the United States (Bayley and Muehlberger, 1968) de-

TABLE 56.—*Some known deposits of helium in the United States and Canada*

State or province	Field (except last entry, which is a well)	Age and name of host rock	Concentration (percent)			Geologic associations	
			He	N_2	CO_2	Possible source rocks	Remarks
Large reserves [1] (1 trillion cubic feet or more of natural gas)							
Kansas, Oklahoma, Texas.	Hugoton	Permian (Wolfcampian) Herington and Krider Limestone Members of Nolans Limestone, Winfield and Fort Riley Limestones, and Towanda Limestone Member of Doyle Shale and equivalents.	0.3–1.9	11.1–41.4	0.1– 1.7	Dark shales of the Permian section.	Hugoton embayment of the Anadarko basin.
Texas	Panhandle	Permian (Wolfcampian) equivalent to Herington and Krider Limestone Members of Nolans Limestone and Winfield and Fort Riley Limestones. Pennsylvanian granite wash.	.1–2.2	3.4–54.7	0–11.7	Uraniferous asphaltite and basement igneous rocks.	On Amarillo-Wichita uplift.
Kansas	Greenwood	Pennsylvanian (Virgilian) Topeka Limestone and (Missourian) Lansing Group.	.4– .7	3.9–28.3	0– 3.1	Rocks equivalent to Heebner Shale Mbr of Oread Ls below reservoir beds.	Adjacent to the west edge of Hugoton field.
Oklahoma	Keyes	Pennsylvanian (Morrowan) Keyes sand of subsurface usage.	.3–2.7	9.6–33.3	.1–16.8	Dark shales of Morrowan age.	On the Cimarron uplift updip from Greenwood field.
Moderate or small reserves [1] (less than 1 trillion cubic feet of natural gas)							
Texas	Cliffside	Permian (Wolfcampian) equivalent to Herington and Krider Limestone Members of Nolans Limestone.	1.7–1.8	23.0–25.2	0.4– 0.8	Uraniferous asphaltite in reservoir rocks.	On the Amarillo uplift.
Kansas	Otis-Albert	Cambrian-Ordovician basal sand (Cambrian Reagan(?) Sandstone).	1.2–2.3	9.1–31.0	.1– .4	Precambrian granite, schist and quartzite.	On Central Kansas uplift.
Colorado	Model Dome	Permian Lyons(?) Sandstone	6.7–8 3	75.7–77.9	13.9–14.8	Precambrian crystalline rocks.	On Apishapa uplift.
New Mexico	Hogback	Pennsylvanian Hermosa Formation.	1.4–8.0	16.5–79.9	.1–20.3	Deep-seated igneous intrusion.	Volcanic necks and dikes in the area.
	Rattlesnake	Mississippian Leadville Limestone and Devonian Ouray Limestone.	7.6–8.0	71.3–76.6	1.9– 3.8	---do	Do.
Arizona	Pinta Dome	Permian Coconino Sandstone	6.6–9.8	86.3–93.7	0– .9	---do	Igneous plugs and dikes in the area.
Utah	Lisbon	Mississippian Leadville Limestone.	.3–1.1	6.7–17.7	21.1–31.3	Mississippian and Devonian shales and Pennsylvanian Molas Formation and regolith.	Gas in Pennsylvanian Hermosa Formation has very little He.
	Harley Dome	Jurassic Entrada Sandstone	7.0	84.5	1.0	Precambrian rocks	On Uncompahgre uplift.
	Woodside Dome	Permian Coconino Sandstone	1.3	64.0	30.0	---do	On San Rafael Swell.
Wyoming	Tip Top	Ordovician Bighorn Dolomite	.8	6.5	85.5	---do	From one well that penetrates thrust plate.
Montana	Cabin Creek	Cambrian sandstone	.4	89.3	.7	---do	Fault and fractures on west flank.
SW. Saskatchewan, Canada.	Wilhelm well 1–9	Cambrian siltstone and mudstone.	1.0–2.0	96.0		---do	Gas at 200 ft above Precambrian erosion surface.

[1] Identified deposits from which gas can be extracted profitably with existing technology and under present economic conditions.

fine broad areas of uplift in much of the country where helium might be expected to accumulate.

The principal submarginal resources of helium are in the earth's atmosphere, where the average helium content is about 5 ppm (Rankama and Sahama, 1950). Even at this low concentration, the total quantity in the atmosphere is about 690 trillion cubic feet.

PROBLEMS FOR RESEARCH

Analyses of the uranium and thorium content of igneous and metamorphic rocks underlying the sedimentary rock section would be useful in identifying the sources and explaining the distribution of helium in natural gases. The basement rock map of the United States (Bayley and Muehlberger, 1968) shows the locations of wells that have penetrated the sedimentary rocks to the basement.

The many thousands of analyses of natural-gas samples made and published by the U.S. Bureau of Mines since World War I are a store of data that lends itself to a statistical approach in the investigation of the origin, occurrence, and distribution of helium.

In gases unsuitable for fuel because of high nitrogen or carbon dioxide content, evaluation of helium resources is a problem because of lack of further drilling after the original discovery wells. Such gases represent some of the best potential resources, and proved reserves of helium possibly could be established with further drilling.

In much natural gas used as fuel, helium is not being recovered and thus is wasted. Most helium is now recovered in big plants located where a large flow of pipeline gas from an extensive producing area can be diverted through the plant. If a better

and cheaper method could be found for recovering helium, then smaller plants could be built in scattered gas fields to recover helium that is now being wasted.

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IRON

By Harry Klemic, Harold L. James, and G. Donald Eberlein

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ABSTRACT OF CONCLUSIONS

Iron is the principal metal employed in modern industrial civilization and is indispensable to everyday living. Annual world production of iron ore is approximately 750 million long tons. The United States produces more than 80 million tons of iron ore per year, of which about 80 percent is from the Lake Superior region. World trade in iron ore is nearly 300 million tons per year and is highly competitive. The United States has sufficient reserves and potential resources of iron ore to meet its needs for many decades but imports about one-third of the iron ore it consumes. Most of the imports are from Canada and South America.

The principal iron-ore minerals are the iron oxides—magnetite, hematite, and goethite. Bedded sedimentary deposits of these minerals in Precambrian banded iron-formations containing 30 percent or more of iron are the principal sources of iron ore. The six major continents contain vast known iron-ore resources. Identified world resources of iron ore, including reserves, exceed 780,000 million tons. Iron-ore reserves in the United States are about 9,000 million tons, and total identified U.S. iron-ore resources, including reserves, are 100,600 million tons. These are mainly in the

Lake Superior region, in low-grade ores that require beneficiation and agglomeration to make them usable.

Research is needed to appraise the economic potential of domestic iron-ore deposits, to develop better techniques for utilizing low-grade ores, and to minimize environmental problems resulting from mining and processing the ores.

INTRODUCTION

Iron is the principal metal employed in modern industrial civilization. It is an abundant and readily extractable gray metal that has a favorable combination of physical characteristics such as hardness, strength, and durability combined with properties that make possible its fabrication into a myriad of useful forms. Alloying of iron and other elements to form steels, in which one or more of the desirable properties of iron are greatly enhanced, has greatly extended the usefulness of the metal. In addition to its many applications in metallic form as steel, iron is combined chemically with many other elements to produce many useful compounds.

The history of man in terms of use of materials has progressed from the stone age through the bronze age through the iron age, and even though the present period is sometimes referred to as the atomic age, iron in the form of steel still is a basic necessity in the technological fabric of nations.

The industrially developed nations of the world could not maintain their present high standards of living without the continued production and use of large quantities of iron and steel products. Nations are ranked in industrial development partly on the basis of total production and per capita consumption of steel. The higher levels in standard of living toward which the peoples of developing nations strive involve ever-increasing use of steel.

Iron and steel have become indispensable in our everyday living. They are used in structural components, transportation equipment, tools, containers, fasteners, pigments, and many other materials. A measure of the sustained use of steel in our economy is indicated by the records of steel production in the United States during the past two decades as shown in figure 33.

This graph tells only part of the story, for it does not indicate steel imports. Large cumulative quantities of iron and steel products are being used in the form of durable items such as bridges, building frames, pipelines, railroads, wire, and countless other items that perform their functions for decades or longer.

Although other materials, such as wood, aluminum, and plastics, are and may continue to be used as substitutes for steel in some items of manufacture, there are no practical substitutes for iron and iron alloys—steel—for a broad spectrum of purposes. The development of special varieties of steel, however, has reduced the amount of steel needed for many purposes. Stronger steel for structural purposes, such as in building frames and bridges, provides equal or greater strength with less material than ordinary steel, and corrosion-resistant steels used in place of ordinary steels have extended the period of usefulness of other items. The recycling of scrap metal has also reduced the amount of primary metal required to meet demand. Consumption of iron and steel scrap in the United States in 1971 was estimated to be more than 80 million short tons (U.S. Bur. Mines, 1972).

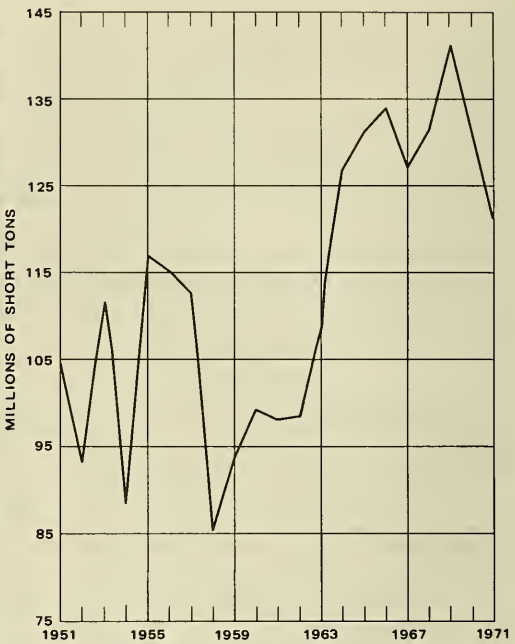

FIGURE 33.—Steel production in the United States, 1951–71. Data from U.S. Bureau of Mines Minerals Yearbooks (1951–70) and Commodity Data Summaries (1972).

World production of iron ore has trebled during the past two decades, rising from 250 million long tons in 1950 to approximately 750 million tons in 1971, as shown in figure 34. Also shown in figure 34 is world trade in iron ore, which has more than doubled since 1955. During the same period annual domestic production of iron ore in the United States has fluctuated between about 60 million tons and

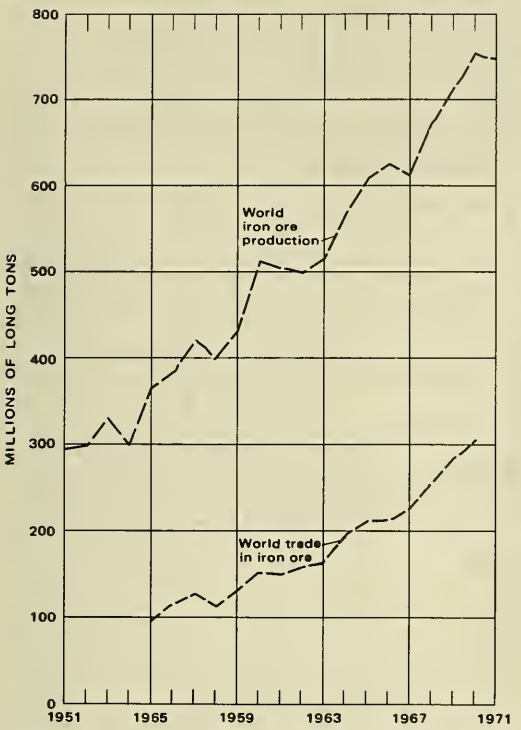

FIGURE 34.—World production and world trade in iron ore since 1951. Data from Institute of Geological Sciences (1971) and from U.S. Bureau of Mines Minerals Yearbooks (1951–70) and Commodity Data Summaries (1972).

118 million tons and in recent years has been between 80 and 90 million tons. This is considerably lower than it was two decades ago, despite an increase of nearly 20 percent in domestic consumption.

A considerable amount of the world trade in iron ore has resulted from the investment of American capital overseas. This has helped to provide the United States with a continuing supply of high-grade, low-cost iron ore, but it has also enabled other nations to obtain assured supplies and to produce fabricated products that compete effectively with American goods, both in the domestic market and in foreign markets that formerly were dependent on U.S. sources.

For many years the United States led the world in iron-ore and steel production. However, in 1958, the Soviet Union surpassed the United States in annual iron-ore production, and in recent years its production has been almost double that of the United States, (U.S. Bur. Mines Minerals Yearbooks 1958–70). Similarly, the United States led the world in steel production until 1971, when it was surpassed by the Soviet Union (Deily, 1972). Japan's steel production has risen to a level equal to 80 percent of that of the United States. The steel industry in the Soviet Union is based wholly upon domestic resources. In contrast, that of Japan is almost entirely dependent upon imports of both iron ore and fuel, yet Japan is a net exporter of steel products to the United States.

The United States has sufficient reserves and potential resources of iron ore and has the productive capacity to meet its needs for iron and steel for many decades. However, for economic and other reasons, the United States is a net importer of finished steel and iron ores. The domestic consumption, production, amounts produced in the Lake Superior region of the United States, and imports of iron ore for consumption in the United States in the period 1951–71 are shown in figure 35.

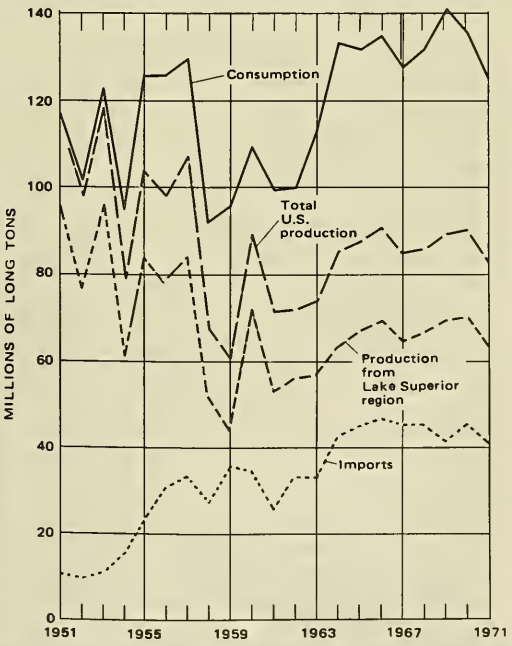

FIGURE 35.—U.S. iron-ore consumption, production, and imports for consumption in the period 1951–71. Data from U.S. Bureau of Mines Minerals Yearbooks (1951–70) and Commodity Data Summaries (1972) and Wimpfen (1971).

In recent years approximately one-third of the iron ore consumed in the United States has been imported (Wimpfen, 1971). About 50 percent has come from Canada, about 40 percent from South America, 5 percent from Africa, and the remainder from Australia, western Europe (mostly from Sweden), Asia, and Oceania. No iron ore is imported from the eastern European countries or from eastern continental Asia. The sources and quantities of imports of iron ore to the United States during the past decade are indicated in figure 36.

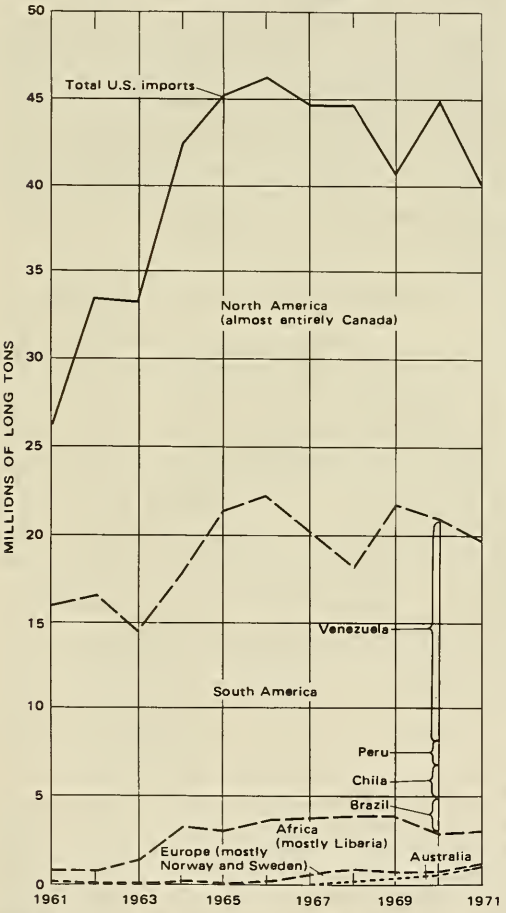

FIGURE 36.—Sources and amounts of iron ore imported to the United States, 1961–71. Data from Institute of Geological Sciences (1971) and from U.S. Bureau of Mines Minerals Yearbooks (1961–70) and Commodity Data Summaries (1972).

Canada, Venezuela, Liberia, Chile, Peru, Sweden, and more recently Australia, have been substantial suppliers of iron ore to the United States. The value of iron ore imported to the United States has exceeded 400 million dollars per year in recent years, while the value of iron ore exported from the United States has been less than 70 million dollars per year, as shown in figure 37.

FIGURE 37.—Value of United States imports and exports of iron ore, 1951–71. Data from U.S. Bureau of Mines Minerals Yearbooks (1951–70) and Commodity Data Summaries (1972).

EXPLOITATION

Iron ore has been produced in 45 of the 50 States of the United States (Dutton, 1955; United Nations, 1970; see also data in U.S. Bur. Mines Minerals Yearbooks 1932–70 and U.S. Geol. Survey and U.S. Bur. Mines Mineral Resources of the United States 1882–1931). Only Kansas, Louisiana, Nebraska, North Dakota, and Hawaii have no record of iron-ore production.

Iron furnaces were built in Virginia and Massachusetts in the 1600's, and before the Civil War furnaces using local iron ores were producing in most of the Eastern States, as reported in early volumes of Mineral Resources of the United States. Quantitative data on production for the early period of American history are scarce, but in 1854, production of iron was about 657,000 tons. This probably required approximately 1.5 million tons of ore.

Iron-ore production increased slowly prior to the Civil War, but between 1870 and 1917, it more than doubled in each 15-year period. Annual production has reflected trends in the business cycle and periods of high wartime demand, as indicated in figure 38.

The rate of growth of domestic iron-ore production has been greatly changed by the increase in imports, as shown in figure 35.

The significance of iron-ore production in the Lake Superior region is evident in the record of ore shipments. Production from the Marquette iron Range began in 1854, from the Menominee Range in 1877, and from the Gogebic Range in 1884; by 1890 the Lake Superior mines furnished 56 percent of the total output. The first shipments from the Mesabi Range were in 1893, and with a few years the Mesabi Range attained a position of dominance that has been maintained to the present. By 1907, 80 percent of the national production was from the Lake Superior region. Total production through 1970 from this region exceeded 4,000 million tons, two-thirds of which was from the Mesabi Range.

Iron-ore shipments in the United States since 1910 have exceeded 4,350 million tons, of which about 81 percent has been produced and shipped from the Lake Superior region (Alm and Trethewey, 1971; Am. Iron Ore Assoc., 1970; see also data in U.S. Bur. Mines Minerals Yearbooks 1932–70 and U.S. Geol. Survey and U.S. Bur. Mines Mineral Resources of the United States 1910–31). The Southeastern States produced about 8 percent, the Western States about 6 percent, the Northeastern States about 4 percent, and the rest of the United States about 1 percent.

Prior to about 1950, most of the material mined and shipped from the Lake Superior region was of

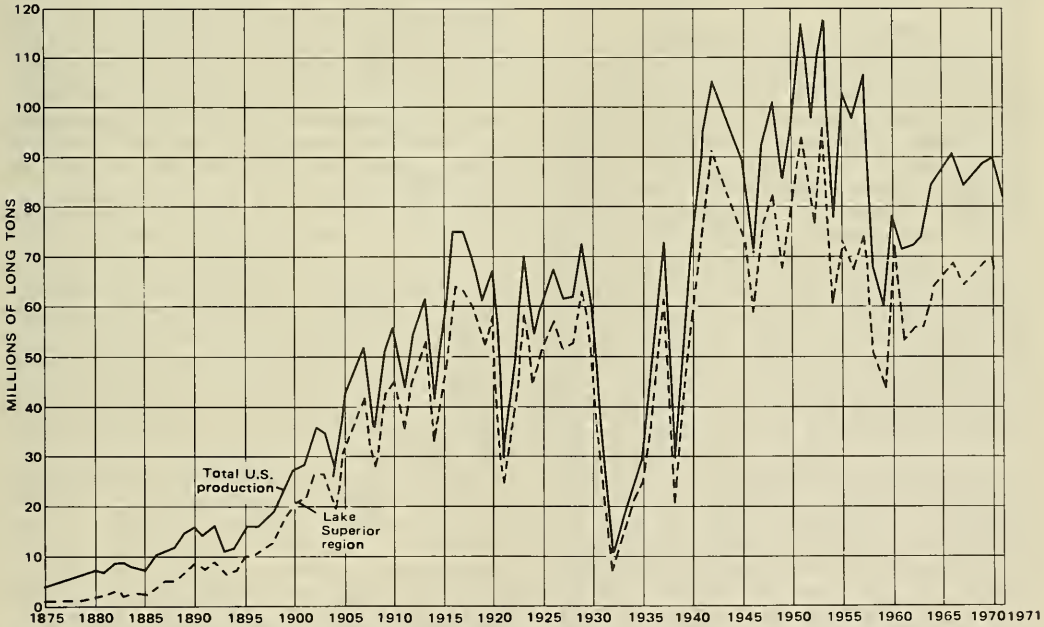

FIGURE 38.—Iron-ore production in the United States and in the Lake Superior region of the United States, 1875–1971. Data from U.S. Geological Survey and U.S. Bureau of Mines Mineral Resources of the United States (1882–1931) and from U.S. Bureau of Mines Minerals Yearbooks (1932–70) and Commodity Data Summaries (1972).

direct-shipping ores or of ores that had been beneficiated by simple washing techniques (Dutton, 1955). As a result of continued large-scale production, resources of direct-shipping ore were rapidly becoming depleted, and efforts were made to obtain alternate sources of ore. Imports were increased rapidly during the 1950's. Since 1964 imports have exceeded 40 million tons per year, as shown in figure 36.

During the 1950's, however, the Lake Superior iron mining industry underwent a technological revolution with the development of processes for large-scale treatment of low-grade material to produce high-grade agglomerates. The agglomerates, principally in the form of pellets, are ideal furnace feed. The net result has been displacement of direct-shipping ore by pelletized concentrates produced from low-grade ores. Jet-drilling, autogenous ore-grinding, magnetic concentration and flotation, and pelletizing now are common practice not only for low-grade ores but also for those of higher grade. The successful research that led to these developments has vastly increased the reserves of minable ore not only in the Lake Superior region but also throughout the world.

BYPRODUCTS AND COPRODUCTS

The banded iron-formations that make up the bulk of the iron resources of the world generally do not contain significant amounts of byproduct or coproduct other than manganiferous iron ore.

Other types of iron deposits, however—particularly those related to igneous activity, some deposits related to surface and near-surface enrichment, and iron-rich placer deposits—commonly contain recoverable or potentially recoverable materials in addition to iron (Dutton, 1955; United Nations, 1970). These are gold, silver, copper, cobalt, titanium, tin, manganese, chromium, nickel, vanadium, zinc, sulfur, phosphates, rare earths, aluminum, fluorine, beryllium, uranium, thorium, and zirconium. In the United States, gold, silver, copper, and cobalt are recovered from iron ore in Pennsylvania and titanium from deposits in New York; phosphate minerals are potentially recoverable from iron deposits in New York and Missouri. Some of these phosphate minerals also contain rare earths, uranium, and thorium. Titanium is recovered from iron sands in Japan, vanadium from iron deposits in South Africa and Peru, and phosphates from deposits in Sweden. Tin may be recoverable from iron deposits in Malaysia and nickel, chromium, and aluminum from lateritic deposits in several tropical areas. Iron has been recovered from nickel ores in Canada and from sulfide-rich copper deposits in the Western United States. Zircon and associated titanium minerals have been recovered from iron-rich sands in Italy.

In addition to the metal and mineral byproducts and coproducts, the waste rock from mining and the tailings from ore beneficiation plants are valuable resources in some areas such as the Northeastern United States. They are used for road metal and for fill for construction purposes, and sand- and gravel-sized materials from some of these plants have been used in making concrete.

ENVIRONMENTAL PROBLEMS

The mining and processing of iron, as with other metals required to sustain the economy, have undesirable environmental consequences. Those specifically associated with iron are chiefly factors of scale: the mines and recovery plants are huge, transportation systems are complex, and furnaces and steel mills are major industries in themselves.

Most of the iron ore produced in the United States is extracted from open pits, which in the Mesabi district are a mile or more wide, many miles long, and several hundred feet deep. The tonnage of waste material produced in stripping operations commonly is two to three times that of the ore mined, and this mass must be disposed of. In the past, most of the waste has simply been accumulated in great unsightly piles adjacent to the mining operation. This spoil could, however, either be returned to mined-out areas or distributed in a beneficial manner. Part of the waste may be processed as low-grade ore.

The pits themselves, after mining ceases, have the potential for environmental enhancement, since most will fill with water and thus become manmade lakes. To make these lakes usable for recreational and other purposes, however, the bounding walls would have to be reduced to a stabilized configuration to protect against hazardous slumping and to provide access. The cost would be substantial, and careful planning before and during the mining operation would be necessary. The added cost would place the domestic industry at a competitive disadvantage with less restrained foreign producers, but at the national level it would yield lasting benefits to the present and future population of the country.

Perhaps a more difficult problem is posed by disposal of the large amounts (more than 50 million tons per year) of finely ground waste (fines) produced in the United States in the extraction process whereby taconite containing about 30 percent iron is concentrated to a product containing 60 percent

or more iron. The traditional method is to deposit this waste, which initially is in the form of a slurry, in settling ponds. The waste itself is not chemically reactive—it consists mainly of quartz—but because of the fine grain size the settled material effectively chokes off organic life. No satisfactory alternative for large-scale disposal or utilization of this material has yet been devised, and the problem deserves intensive research.

GEOLOGIC ENVIRONMENT

Iron is one of the more abundant and ubiquitous elements in the earth's crust. Common sedimentary rocks contain 2–3 percent iron and basalt and gabbro contain about 8.5 percent; the average content of crustal rocks is about 5 percent. Rock mined economically ranges in iron content from about 20 percent to 69 percent, so the concentration factor ("concentration clarke") relating crustal abundance to minable ore is very low—4–14, as compared with factors of 10^2 or 10^3 for elements such as manganese, chromium, copper, and lead (James, 1966).

The ability of iron to exist in more than one valence state, coupled with its general abundance, accounts for the presence of iron minerals in deposits of widely different character and associations. The geochemical cycle of iron is complex, but it is reasonably well known and contains may points at which the element can be trapped to form significant concentrations. Economically minable deposits are formed by magmatic segregation, hydrothermal replacement, direct sedimentation and diagenesis, and weathering processes at the surface and in the subsurface.

ORE MINERALS

Nearly 300 minerals contain iron as an essential component, but only about six of them can be classed as ore minerals, and of these only the oxides—magnetite, hematite, and goethite (limonite)—are of major importance (Gross, 1965; James, 1966; United Nations, 1970). Siderite (the iron carbonate), pyrite and pyrrhotite (iron sulfides), and chamosite (an iron silicate) are mined locally, but deposits of these minerals are at present of minor economic significance. Ilmenite, the iron-titanium oxide, is a potential source of byproduct iron, but it cannot be classed at this time as an iron-ore mineral.

The ore minerals are listed as follows:

Magnetite (Fe_3O_4).—Black, strongly magnetic. Iron content, 72.4 percent. Principal ore mineral of those parts of Precambrian banded iron-formations mined as taconite; associated with quartz and generally minor amounts of iron carbonate and iron silicates. Principal ore mineral of replacement deposits, in which associated minerals vary with type of deposit but commonly include specularite, pyrite, and pyrrhotite, and silicates such as garnet and actinolite.

Hematite (Fe_2O_3).—Black (if coarse) to red (if fine), depending upon grain size; virtually nonmagnetic. Iron content, 70 percent. As specularite, a common and locally important ore mineral with magnetite in taconite and in replacement deposits. As red iron oxide, a principal constituent of secondary (direct-shipping and semitaconite) deposits in Precambrian iron-formations, associated with goethite (limonite), and in younger sedimentary oolitic ironstones, associated with goethite, calcite, and clastic quartz.

Goethite ($Fe_2O_3 \cdot H_2O$).—Yellow to dark brown, commonly soft and earthy, may be hard and brittle; nonmagnetic. Iron content, about 60 percent. Limonite is the general term applied to earthy or impure goethite. Principal constituent of ores originating by surface or near-surface weathering processes, as in laterites; associated minerals mainly hematite and clay minerals.

Siderite ($FeCO_3$).—Gray, but exposed material quickly acquires tan or reddish color owing to surface oxidation; nonmagnetic. Iron content of pure mineral is 48 percent, but in most siderite the iron is replaced by significant amounts of manganese, calcium, or magnesium. A major constituent of Precambrian iron-formations and of some younger ironstones, but in North America mined as an iron ore only in the Michipicoten district of Ontario, where it is associated with pyrite.

Pyrite (FeS_2) *and pyrrhotite* ($Fe_{1-x}S$).—Yellow, with metallic luster; pyrrhotite is weakly magnetic. Pyrite is a principal mineral in the relatively scarce sulfide facies of Precambrian iron-formations and younger ironstones; mined as an iron ore in North America only in the Michipicoten district of Ontario (see above). Surface oxidation of pyrite and pyrrhotite bodies gives rise to deposits of iron oxides that have been mined locally.

Chamosite ($(Mg,Fe,Al)_6(Si,Al)_4O_{14}(OH)_8$). —Greenish, fine-grained, chloritelike; nonmagnetic. Major constituent of post-Precambrian oolitic ironstones; locally mined as ore in Europe, associated with siderite and goethite.

CLASSIFICATION OF DEPOSITS

The ores of iron fall into four main categories, based on mode of origin (James, 1966). The genetic classification outlined below is basically geologic

rather than economic, but it does, however, provide a practical means of grouping characteristics such as mineralogy, tonnage-grade factor, form, and projection in depth, that are of prime importance to assessment of resource potential. The major categories, together with the more significant subdivisions, are listed as follows and are discussed in more detail in succeeding paragraphs.

I. Bedded sedimentary deposits:
   A. Banded iron-formations, almost exclusively Precambrian.
   B. Ironstones, mainly post-Precambrian.
   C. Miscellaneous sedimentary deposits, including "black band" siderite, bog iron, and clastic accumulations.
II. Deposits related directly to igneous activity:
   A. Magmatic segregations.
   B. Pyrometasomatic deposits.
III. Deposits formed by hydrothermal solutions:
   A. Replacement deposits in nonferruginous rocks.
   B. Enrichments of preexisting ferruginous rocks.
IV. Deposits produced by surface or near-surface enrichment:
   A. Laterites.
   B. Enrichments of low-grade ores.

BEDDED SEDIMENTARY DEPOSITS (I)

The principal concentrations of iron in the earth's crust are products of chemical sedimentation, which have been modified by wave and current action, by chemical and mineralogic changes that take place below the depositional interface (diagenesis), and by mineralogic changes induced by heat and pressure in burial environments.

BANDED IRON-FORMATIONS (I-A)

Banded iron-formations occur as sedimentary units in Precambrian rocks throughout the world. They constitute the greatest single source of iron now being mined and contain the largest potential resources. The rock has been defined as follows: "a chemical sediment, typically thin bedded or laminated, containing 15 percent or more iron of sedimentary origin, commonly but not necessarily containing layers of chert." In some iron-formations the iron is in the form of carbonate(siderite, with an appreciable content of manganese, magnesium, and calcium) or silicate (greenalite, minnesotaite, stilpnomelane), and in rare occurrences it is in the form of sulfide (pyrite). The most distinctive and economically most significant rock type, however, consists of iron oxides (magnetite or hematite) and chert (or its recrystallized equivalent) in alternating thin layers, with an iron content commonly in the range of 25 to 40 percent. Each of the sedimentary facies—oxide, carbonate, silicate, sulfide—has the distinctive aspects of mineralogy, total iron content, and structure that are summarized in table 57.

TABLE 57.—*Principal features of the iron-formation facies (modified from James, 1966)*

	Sulfide	Carbonate	Silicate		Oxide	
			Nongranular	Granular	Magnetite-banded	Hematite-banded
Lithology	Laminated to thin-banded black pyritic carbonaceous slate. Chert rare.	Thin-bedded to laminated rock consisting of alternating layers of gray chert and carbonate.	Laminated light-green to greenish-black rock. Chert rare.	Massive dark-green rock with irregular bedding marked by layers of chert and magnetite.	Dark, thin-bedded to irregularly bedded rock consisting of layers of magnetite alternating with layers of dark chert, green silicates, or silicates plus carbonate.	Thin-bedded to irregularly bedded rock consisting of alternate layers of crystalline hematite and gray chert or reddish jasper.
Principal iron mineral.	Pyrite	Iron-rich carbonate	Iron silicate (minnesotaite, stilpnomelane, chlorite).	Iron silicate (greenalite, minnesotaite, stilpnomelane).	Magnetite	Crystalline hematite.
Subsidiary iron minerals (rarer minerals in parenthesis).	Carbonate (Greenalite).	Pyrite, stilpnomelane, minnesotaite, magnetite (hematite).	Carbonate, magnetite.	Magnetite, carbonate, hematite.	Greenalite, minnesotaite, stilpnomelane, carbonate, hematite (pyrite).	Magnetite (carbonate).
Typical range in content of metallic iron, in percent.	15–25	20–35	20–30	20–30	25–35	30–40
Distinctive features.	Graphitic	Stylolites common	Laminated structure.	Granule-bearing	Strongly magnetic	Locally oolitic.
Environment of origin.	Strongly reducing, anaerobic.	Reducing	Variable, but typically mildly reducing.	Mildly oxidizing to mildly reducing.	Mildly oxidizing to mildly reducing.	Strongly oxidizing.

Many iron-formations have undergone conditions of higher temperature and pressure (metamorphism) which have changed preexisting minerals to silicates such as grunerite, pyroxene, and olivine and which have resulted in coarsening of grain size of quartz, magnetite, and hematite. Oxide facies of iron-formation that has been so metamorphosed is the most suitable as a low-grade ore (taconite) because the iron oxides are more readily concentrated by milling. In contrast, the more weakly metamorphosed carbonate and silicate facies, generally not usable at the present time in the United States as low-grade ore, are more susceptible to alteration by surface and ground waters and commonly give rise to ore bodies of soft limonite and hematite (direct-shipping ores) and to deposits classed in the Lake Superior region as "wash ores" or "semi-taconite" (Dutton, 1955; United Nations, 1970).

Chemically, the iron-formations are marked by extraordinarily low contents of alumina, sodium, potassium, and minor elements. Iron and silica generally dominate, but in some districts, notably the Cuyuna district of Minnesota, the manganese content is several percent (Dutton, 1955).

The banded iron-formations commonly are exposed as steeply to moderately dipping beds in belts a few miles to several tens of miles long (Gross, 1965). A few, such as those in Labrador, are in belts several hundreds of miles long. Thicknesses commonly are on the order of a few hundred feet but range from less than 25 to more than 2,000 feet. With some prominent exceptions, notably the Mesabi Range of Minnesota and the Hamersley Range of Australia, the iron-formations are tightly, and often very complexly, folded. Dips generally are 60° or more, a fact of considerable importance to economic assessment. Aggregate tonnages of rock containing 20 percent or more iron are enormous, but factors such as location, mineralogy, and structure are of profound importance in assessment of actual potential.

Prominent examples of this class of iron deposits are the iron ranges of the Lake Superior region of the United States—Mesabi, Cuyuna, Gogebic, Marquette, and Menominee; the Michipicoten, Lake Albanel-Mistassini, and Labrador districts of Canada; the Quadrilátero Ferrífero of Brazil; the Krivoi Rog and Kursk districts of Russia; and the Hamersley Range of Australia (James, 1966; United Nations, 1970).

IRONSTONES (I-B)

The strata classed as ironstones contain iron in grades comparable to or greater than that of Precambrian banded iron-formations—that is, in the general range of 20–40 percent—but they differ profoundly in many ways, notably in much younger age, in the absence of interlayered chert, and in the much smaller dimensions (James, 1966).

Considerable variety exists within the class, but the most common type is thick-bedded rock consisting of small pellets (ooliths) of limonite, hematite, or chamosite in a matrix of chamosite, siderite, or calcite. Grains of clastic quartz and fossil fragments form the cores of many ooliths and are dispersed in the matrix, and the acceptability as an ore depends in part on the relative amounts of quartz and calcite. Rock containing abundant calcite may be self-fluxing, whereas content of abundant quartz is deleterious. Phosphate minerals are also common contaminants in ironstones. As with banded iron-formations, ironstones may be divided into oxide, carbonate, silicate, and sulfide facies, depending upon the dominant iron mineral. The rocks originate as chemical sediments, but the oolite types—economically the most important—have been profoundly modified by wave action and transport so that chemically heterogeneous assemblages of limonite (or hematite), chamosite, and siderite are common.

Thicknesses of ironstone formations range from at least a foot to several tens of feet. Beds tend to be lenticular on a scale of a few thousand feet or a few miles, but a belt of deposits having approximately the same age may continue for hundreds of miles, as for example those in the Clinton Formation of Silurian age that extend from Alabama to New York. In general, thicknesses and lateral extents of ironstones are an order of magnitude less than those of banded iron-formations, consequently potential tonnages probably are less than 1 percent of those contained in the older rocks.

Because of the prime importance of location, ease of beneficiation, and local near-surface enrichment, many ironstones have been and are being mined. The relative importance of these ores in world production, however, is decreasing. The most important region of economic extraction was in northern Europe—England, France, Luxembourg, and Germany—where the ironstones of Jurassic age have been mined for generations. In North America, the most important examples have been the Clinton ores of Silurian age in the Birmingham district of Alabama and the Wabana ores of Ordovician age in Newfoundland (United Nations, 1970).

MISCELLANEOUS SEDIMENTARY DEPOSITS (I-C)

Iron has been extracted in the past from a variety

of sedimentary rocks other than banded iron-formation and ironstone, but these are of little present or potential importance. Bog-iron deposits, which are accumulations of iron oxides in swampy areas or shallow lakes in northern latitudes, have been mined in northern Europe and North America (James, 1966).

"Black band" and "clay band" are deposits of siderite that occur as thin layers in coal sequences; they once were mined extensively in Great Britain. Possibly of greater potential significance are clastic accumulations of iron minerals (black sands) such as occur in southeastern Alaska and New Zealand; these, however, typically contain abundant ilmenite, the iron-titanium oxide, and recovery of iron depends upon the economic feasibility of separation and recovery of titanium (United Nations. 1970).

DEPOSITS RELATED DIRECTLY TO IGNEOUS ACTIVITY (II)

Iron may be concentrated during crystallization of igneous rocks in several ways: (1) as a constituent of early formed minerals such as ilmenite that may have settled to the base of the magma chamber, (2) as a late-stage magmatic fraction from which iron minerals are precipitated after most other constituents have crystallized, and (3) as a constituent of fluids (gases and aqueous liquids) that escape the magma chamber and deposit iron minerals in surrounding rocks (James, 1966). The first two constitute category II-A; the third (and quantitatively probably most important), category II-B.

MAGMATIC SEGREGATIONS (II-A)

Magmatic segregations of iron fall into two main groups: titaniferous and nontitaniferous.

The titaniferous ores occur as layers and segregations in gabbro, pyroxenite, and anorthosite. The deposits in gabbro and pyroxenite commonly are crudely layered lenses of magnetite, ilmenite, and silicates such as pyroxene. Content of iron generally is about 20 percent, and that of titanium is 2 percent or more. Many of these deposits, particularly in Alaska, are of considerable thickness and extent, but as with the titaniferous black sands referred to previously, their significance as potential sources of iron hinges largely on the feasibility of separating iron from titanium economically (United Nations, 1970). Most of the ores occurring in anorthosite are of quite different character. These are irregular masses and dikes of coarse-grained ilmenite, magnetite or specularite, feldspar, ulvospinel (Fe_2TiO_4), and rutile (TiO_2), often in complex intergrowths on a microscopic scale. Deposits are abundant in the belt of Precambrian anorthosite bodies that extends from upper New York State northward into Quebec and Labrador. The iron content of some deposits, such as the one at Allard Lake, Quebec, is about 40 percent, but the ore is exploited primarily for titanium and iron recovered as a byproduct.

Nontitaniferous magmatic segregations are not abundant in North America, but they form the great ore bodies of the Kiruna, Rektor, and other districts of northern and central Sweden (United Nations, 1970). These Swedish deposits occur within syenite porphyry and quartz porphyry as massive sheets or irregular veinlike masses composed of magnetite and minor amounts of hematite. The main body at Kiruna is a steeply dipping sheet several hundred feet thick and at least 14,000 feet long. The iron content is 60–65 percent. Phosphorus content is high, commonly 1–2 percent, and this may have been a significant factor in the evident ability of a concentrated iron fluid to separate, remain molten, and ultimately intrude solidified parts of the parent igneous body.

The important ore bodies of Precambrian age in Missouri, such as those at Pea Ridge and Pilot Knob, are similar in occurrence and association to the Kiruna deposit and are so classed in this report. Some marginal parts of these ore bodies, however, show indications of hydrothermal activity, and there may well be all gradations between a purely magmatic concentration and a high-temperature hydrothermal transfer of iron to form replacement ore deposits in peripheral rocks.

PYROMETASOMATIC DEPOSITS (II-B)

This category encompasses a rather wide variety of deposits that have igneous (presumably genetic) associations ranging from diabase to syenite.

The typical pyrometasomatic or contact metamorphic deposits are replacements, most commonly in limestone, at or near a contact with the parent igneous rock. An important group in the United States is related to Triassic diabase sills that occur in a belt that extends intermittently from Connecticut to South Carolina. The known deposits of iron ore, however, are restricted to a 75-mile segment that centers at Cornwall, Pa. (Carr and others, 1967). The deposit at Cornwall, which has been mined since 1792, is the type example; here the ore occurs in two separate bodies replacing limestone of Cambrian age (Dutton, 1955). The ore bodies are tabular masses about 100 feet thick and half a mile to a mile long, and they extend downdip for as much as 2,400 feet. The ore contains about 40 percent iron

as magnetite, which is associated with sulfides, among which pyrite and chalcopyrite are dominant. Actinolite and chlorite are the chief gangue minerals. Copper, silver, gold, and cobalt are recovered as byproducts (United Nations, 1970). Elsewhere in Pennsylvania, similar ore deposits are found in Precambrian marble and in Triassic limestone conglomerate in each case in close proximity to a sheet of diabase. The relationship between diabase, limestone, and ore is incontrovertible, but the precise origin of the ore-forming fluids is less evident.

Pyrometasomatic ore bodies related to quartz monzonite are fairly common in the Rocky Mountain region of the United States, and some are of large dimensions (Carr and others, 1967; United Nations, 1970). The mined deposits of the Iron Springs district, Utah, occur at or near the contacts of laccolithic bodies of quartz monzonite of Tertiary age with limestone of Jurassic age. Dimensions are on the order of a thousand feet in strike and dip length, with thicknesses of as much as 230 feet. The iron content is about 50 percent, and the iron is in the form of magnetite. Gangue minerals include phlogopite and fine-grained calc-silicates, and significant amounts of apatite; phosphorus content is as much as 5 percent in places and averages 0.2 percent. The ore was deposited by fluids emanating from the intrusive quartz monzonite.

DEPOSITS FORMED BY HYDROTHERMAL SOLUTIONS (III)

Many iron deposits are hydrothermal in origin—that is, they were deposited by heated aqueous fluids. These fluids may have originated from relatively distant bodies of crystallizing magma, or they may simply represent waters of any origin that have circulated at depth to acquire the necessary heat. Similarly, the iron may be of primary origin from a magma, or it may have been leached from rocks being traversed by the solutions. The deposits of hydrothermal origin can be divided into two general groups: those in which the iron has been derived from a distant source, then transported and deposited in virtually nonferruginous rocks; and those in which the ores represent a further concentration of iron in rocks that are themselves relatively iron rich.

REPLACEMENT DEPOSITS IN NONFERRUGINOUS ROCKS (III-A)

Deposits of small to medium size are common in areas of relatively recent magmatic activity, as in the Western United States, and a genetic relation generally is inferred. Most occur as pods, veins, and lenses in volcanic rocks, brecciated igneous rocks, and limestone (Carr and others, 1967; Dutton, 1955; United Nations, 1970). Magnetite and hematite are the typical ore minerals and occur mainly in association with pyrite and chalcopyrite, but some veins and bedding replacements consist wholly or largely of siderite. The largest production in the Western States—several million tons—from deposits of this category has been from the Buena Vista Hills district of Nevada. Here the ore occurs as irregular bodies of magnetite and hematite in metavolcanic rocks and diorite of probable Jurassic age. The host rocks are extensively altered to scapolite, a distinctly unusual feature in ore deposits of this type. Individual ore bodies in the Nevada deposits have maximum strike and dip lengths of several hundred feet, and widths rarely exceed 100 feet.

An unusual group of deposits assigned to this category is that of Precambrian age in New York and New Jersey (Carr and others, 1967). The ore bodies are tabular to pencillike masses of magnetite and hematite oriented along the dominant linear structure of the enclosing gneiss. The largest known ore body is at the Benson mine, New York, on the overturned flank and keel of a syncline; it has been mined for a strike length of 2½ miles and has been traced magnetically for an additional 5 miles. Mining widths are several hundred feet. Ores of this group of deposits commonly are relatively low grade; the ore at the Benson mine averages about 23 percent iron, and contacts with the country rock are gradational. Gangue minerals are dominantly those of the enclosing gneiss: quartz, potassium feldspar, sillimanite, garnet, and ferromagnesian minerals. Some of the ore contains appreciable amounts of titanium minerals. Structurally, these deposits have features in common with those of category III-B (see below), but no convincing evidence for an original bed of iron-rich rock has been presented; if one existed, the high titanium content suggests that it was deposited as a black sand rather than as a chemically precipitated sedimentary iron-formation.

ENRICHMENTS OF PREEXISTING FERRUGINOUS ROCKS (III-B)

In several places in the world, most notably in the Quadrilátero Ferrífero of Brazil, very large deposits of high-grade ore occur within beds of Precambrian iron-formation (United Nations, 1970). The ore consists of crystalline hematite (specularite) with minor magnetite, locally with retention of the thinly layered structure of the original iron-formation. Some of the ore is loose and friable. The iron content approaches 70 percent, the theoretical content of pure hematite, and reserves exceed a billion tons. The deposits are believed to have originated by

hydrothermal replacement of silica layers along favorable structures in the enclosing iron-formation, but the source of the solution is unknown. Deposits of similar character occur in Liberia, Mauretania, India, Australia, and in the now dormant Vermilion district of Minnesota.

DEPOSITS PRODUCED BY SURFACE OR NEAR-SURFACE ENRICHMENT (IV)

Many iron deposits owe their origin to surface or near-surface enrichment of rocks of lesser iron content. Preexisting iron-bearing minerals are attacked by surface and ground waters, and the iron is altered to limonite and hematite, often with the loss of other elements in solution. In localities where surface erosion is minor, or where the oxidation occurs below the surface, the result is a progressive concentration of iron oxides. Many of these residual deposits have been mined in the past, and some that are of major economic or potentially economic importance remain.

Two general groupings are convenient: Laterites, which are characteristic products of weathering in humid tropical climate, and residual enrichments of lower-grade iron deposits.

LATERITES (IV-A)

The process of lateritization is one of deep chemical weathering under tropical conditions with alternating wet and dry seasons. The nature of the product varies with that of the underlying rock; bauxite, for example, is produced by lateritization of rock high in alumina relative to quartz and iron minerals. The iron-rich laterites most commonly are derived from serpentine, as in Cuba and the Philippine Islands (Dutton, 1955; United Nations, 1970). The material is porous and brown, and it may accumulate to depths of many tens of feet. Surface areas are measured in square miles, and so the potential tonnage is very large. The dominant ore mineral is limonite (impure goethite), and the iron content of the rock commonly is 40–50 percent. Nickel, cobalt, and chromium also are concentrated in laterite. The major impurity is clay which, along with chromium, cobalt, and nickel, inhibits the greater use of laterite as an iron ore. Many iron-rich laterites now are being mined for nickel alone, but future improvement of metallurgical techniques may result in greater use of laterite as an iron ore, with nickel and cobalt, and possibly chromium, as coproducts.

ENRICHMENTS OF PREEXISTING LOW-GRADE ORES (IV-B)

Most of the iron ore used in the world to date has been produced from deposits arising from the near-surface enrichment of lower grade material. Before the development of a method for processing taconites, virtually all the production from districts such as the Mesabi in the United States and Krivoi Rog in Russia was of soft limonite and hematite. These direct-shipping ores, with iron contents of 50–60 percent, and the so-called wash ores and semitaconite of the Lake Superior region are products of deep residual enrichment of primary iron-formation, in which oxidation of ferrous minerals was accompanied by partial to complete leaching and replacement of chert (James, 1966). The enrichment extends to considerable depths in many parts of the world—commonly to many hundreds of feet and in some districts to as much as 5,000 feet. The deposits have yielded immense amounts of ore; the Lake Superior districts alone have produced more than 3 billion tons (Alm and Trethewey, 1971; see also data in U.S. Bur. Mines Minerals Yearbooks 1932–1970 and U.S. Geol. Survey and U.S. Bur. Mines Mineral Resources of the United States 1882–1931).

Many other examples exist of ores that are products of enrichment. The famous Bilbao deposits of Spain consist of massive limonite and hematite derived by enrichment of preexisting siderite bodies (United Nations, 1970). The brown ores of Texas and the southeastern United States were formed by oxidation and enrichment of Tertiary strata containing siderite and glauconite. The hard ores of the Marquette district of Michigan, which occur at the top of the Negaunee Iron-formation, probably represent in part a former enrichment and in part a clastic accumulation, now profoundly modified by metamorphism.

SUMMARY OF TYPES OF DEPOSITS

Table 58 presents a general summary description of types of iron-ore deposits. Characteristics such as iron content and form vary widely in each type, but the descriptions given apply reasonably well to the major deposits.

RESOURCES

IDENTIFIED RESERVES AND RESOURCES

Vast quantities of iron-ore resources are known to exist throughout the world. A recent survey of world iron-ore resources by the United Nations (1970) indicated world reserves totaling approximately 250,000 million metric tons and an additional 530,000 million tons of potential iron-ore resources. The estimated iron-ore resources of various parts of the world, slightly modified from the amounts listed above, are shown in table 59.

TABLE 58.—*Summary description of categories of iron ore*

Subdivision and location of typical example	Principal iron minerals	Average of typical iron content (percent)	Form of exploited deposits	Present importance	Resource potential: United States	Resource potential: World
I. Sedimentary deposits						
I–A. Banded iron-formation: Labrador	Magnetite, hematite, siderite, iron silicates.	33	Bed hundreds of feet thick, tens of miles in strike length.	Major	Enormous	Enormous.
I–B. Ironstone: Birmingham, Ala.	Limonite, hematite, siderite, chamosite.	30	Beds tens of feet thick, miles in strike length.	Minor	Medium	Large.
I–C. Miscellaneous (bog iron, black band siderite, black sands):	Limonite, siderite, magnetite, ilmenite.	--	Various	Negligible	Small	Small.
II. Deposits related directly to igneous activity						
II–A. Magmatic segregations: Kiruna, Sweden	Magnetite	65	Tabular bodies, hundreds of feet thick, many thousands of feet long.	Modest	Medium	Medium.
II–B. Pyrometasomatic deposits: Cornwall, Pa.	Magnetite, hematite	45	Tabular to podlike deposits, a few hundred feet thick, a few thousands of feet long.	---do	Large	Do.
III. Deposits formed by hydrothermal solutions						
III–A. Replacement deposits in nonferruginous rocks: Buena Vista, Nev.	Magnetite, hematite, siderite.	30	Irregular pods, lenses, stockworks; veins.	Minor	Small	Small.
III–B. Enrichments of preexisting ferruginous rocks: Minas Gerais, Brazil	Specular hematite, minor magnetite.	68	Tabular bodies parallel or subparallel to bedding of enclosing iron-formation. Thickness up to several hundred feet.	Modest	Negligible	Medium.
IV. Deposits produced by surface or near-surface enrichment						
IV–A. Laterite: Cuba	Limonite, hematite	45	Blankets tens of feet thick, tens or hundreds of square miles in area.	Minor	Small	Large.
IV–B. Secondary enrichments of low-grade iron deposits: Lake Superior (direct-shipping and wash ores).	Limonite, hematite	55	Blankets to sacklike bodies, dimensions in hundreds to thousands of feet. Most restricted to depth of a few hundred feet below surface, but Lake Superior deposits extend to several thousand feet.	Major	Large	Do.

TABLE 59.—*World iron-ore resources, in millions of metric tons, figures rounded (United Nations, 1970)*

Country, region, or continent	Reserves [1]	Identified resources, [2] including reserves
United States	9,000	101,000
North America exclusive of United States (mostly Canada)	36,000	126,000
South America	34,000	94,000
Europe	21,000	34,000
Africa	7,000	31,000
Australia and New Zealand	17,000	[3] 17,000+
Asia	17,000	72,000
U.S.S.R.	111,000	304,000
Total	252,000	779,000+

[1] Reserves: Identified deposits from which minerals can be extracted profitably with existing technology and under present economic conditions.
[2] Identified Resources: Specific, identified mineral deposits that may or may not be evaluated as to extent and grade, and whose contained minerals may or may not be profitably recoverable with existing technology and economic conditions.
[3] Mostly high-grade ores; vastly greater quantities of lower grade iron-formations are known but have not been assessed.

The amounts listed as reserves include large quantities of low-grade ores as well as high-grade ores. Therefore the tonnages listed for the various continents or regions are not directly comparable in terms of iron content. Nevertheless, the total reserve figures, even reduced by two-thirds to compensate for a ratio as low as 3 tons of crude ore to 1 ton of shipping-grade concentrate from taconite ores, represent more than 100 years' supply at recent world iron-ore production rates of nearly 750 million tons per year. The total crude-ore resources, including reserves, represent more than 300 times the recent annual production of shipping-grade ore.

At least four nations in the world—U.S.S.R., Canada, Brazil, and Australia—have ore reserves in excess of 10 billion tons each. Nine—United States, India, France, Peoples Republic of China, Sweden, United Kingdom, Federal Republic of Germany, South Africa, and Venezuela—have reserves of more than 1 billion tons each. Other nations which have substantial iron-ore reserves in production and which have exported more than 500,000 tons a year in recent years are Angola, Chile, Korea (south), Liberia, Malaysia, Morocco, Norway, Peru,

Philippine Republic, Sierra Leone, Spain, and Tunisia.

The identified iron-ore resources of the United States are shown in table 60.

TABLE 60.—*The identified iron-ore resources of the United States, in millions of metric tons (United Nations, 1970)*

[Figures rounded. Include estimates for some deposits for which precise data are not available]

Region	Reserves [1]	Identified resources [2] (reserves + potential ores)
Lake Superior	6,500	78,000
Northeastern	200	1,400
Southeastern	100	9,400
Central-Gulf	600	700
Central-western	1,100	2,300
Western	600	1,200
Alaska	----	6,600
Hawaii	----	1,000
Total	9,100	100,600

[1] Reserves: Identified deposits from which minerals can be extracted profitably with existing technology and under present economic conditions.

[2] Identified resources: Specific, identified mineral deposits that may or may not be evaluated as to extent and grade, and whose contained minerals may or may not be profitably recoverable with existing technology and economic conditions.

HYPOTHETICAL RESOURCES

Because of the great amounts of identified iron-ore resources, no attempt is made to estimate quantities of hypothetical iron-ore resources beyond stating that they are enormous. The identified iron-ore resources in the world are a sampling of the surface and near-surface parts of the geologically explored land areas of the earth. Most of the identified resource material is within half a mile of the surface of the earth. It is reasonable to expect that in many areas the zone between a depth of half a mile and 1 mile beneath the surface will contain hypothetical resources proportional in amount to the near-surface identified quantities. This concept is especially applicable to the great expanses of Precambrian iron-formation and younger ironstone formations that exist on all the continents. It also applies to areas in which deposits are the results of processes related to magmatic activity. Allowance must be made, however, for some deposits that are not resources because they did not undergo surficial enrichment and also for some flat-lying iron-formations that do not extend to depths of more than half a mile.

In North America, and in the geologically explored parts of other continents, bedded Precambrian sedimentary iron-formations and younger sedimentary ironstone deposits extend for lengths totaling hundreds of miles (United Nations, 1970). Undoubtedly these formations, in many areas, maintain their basic characteristics for considerable distances in the subsurface. In view of the existence of very large quantities of identified iron-ore resources, and because setting upper limits to the amounts of hypothetical iron-ore resources would involve many questionable assumptions, detailed estimates of the existing quantities of hypothetical iron-ore resources can have little meaning. Factors such as the amounts of ore that must be left in place as mine pillars and physical limitations upon depths to which mining activities can be carried on in various types of rock impose limitations upon the practical estimation of hypothetical resources at great depths. Advances in the state of the art of mining can extend the depths to which ore can be mined, but can also extend the competitive exploitation of low-grade shallow ore deposits.

SPECULATIVE RESOURCES

Although speculative iron-ore resources are impossible to quantify in any meaningful way, they are worthy of consideration. In the past two decades most of the identified iron-ore resources of Australia became known, and Australia has become one of the major iron-ore producing nations (Inst. Geol. Sci., 1971; United Nations, 1970). Similarly, large high-grade deposits, measuring in thousands of millions of tons, have been identified in recent years in Brazil. Large areas in South America, Africa, Asia, and Antarctica remain to be explored geologically. On the other continents large areas in which Precambrian basement rocks are under a relatively thin cover of younger rocks offer possibilities for the discovery of major iron deposits. Manganese- and iron-rich nodules and other sediments on the sea floor remain to be assessed as potential resources .

In the United States, the most promising regions for iron-ore discovery have largely been identified and at least partially explored. The principal need is to obtain more detailed information concerning these regions. Because most of the major iron deposits or iron-bearing formations have associated magnetic anomalies, major programs of aeromagnetic surveying to delineate the zones of magnetic rocks and potential ore bodies should be continued. Such surveys have been made for many areas and have proved to be successful. In some cases further geologic studies and interpretations of the magnetic and geological data are needed.

EXPLORATION

Exploration for iron ores differs significantly from that involved in the search for most other metals, in part because of the low value of ore—

less than 1 cent a pound—and the general abundance of deposits, and in part because most ores are magnetic or have some surface expression and hence are comparatively easy to discover.

In unexplored areas, now relatively few in the United States, the primary tool in the search for new deposits is the airborne magnetometer. Surveys can be made rapidly and inexpensively; an area of 1,000 square miles can be adequately searched at a cost less than $20,000. Once favorable areas are located, detailed geologic mapping and ground magnetic surveys, possibly supplemented by gravity surveys, serve to delineate target areas for drilling.

Most exploration in the United States except that for buried magmatic, pyrometasomatic, or hydrothermal deposits, is directed not toward discovery but toward definition of deposits that meet the economic criteria of geologic location, large size, suitability for low-cost mining and beneficiation, and low content of objectionable impurities. The major developments of the past 20 years in the United States and Canada and many that are anticipated in the future concern the bedded iron-formations (taconites) in the Lake Superior and the Rocky Mountain regions. The location and extent of virtually all such deposits probably are now known, but intensive geologic mapping, drilling, and sampling are necessary to appraise the actual economic potential. Investments for a major taconite mine and processing plant are so large that a minimum proved reserve of about 100 million tons of minable low-grade ore commonly is required.

Exploration for buried high-grade deposits of magmatic, pyrometasomatic, or hydrothermal origins presents problems more analogous to those encountered in base-metal exploration. The deposits are likely to be irregular in form and size, and they lack the geologic predictability of bedded ores. Nevertheless, those within a few thousand feet of the surface generally will yield measurable aeromagnetic anomalies that provide a basis for restricting the area in which detailed geologic and ground magnetometer surveys are needed for definition of drilling targets.

The geologic and geophysical techniques are used to select targets, but physical sampling and analyses of samples are required to prove the existence of a mineral deposit of economic value. Such sampling commonly involves drilling to obtain representative specimens of the ore from locations sufficiently spaced so as to give a three-dimensional view of the ore zone and thus locate a volume large enough to meet the minimum size requirements for an economically minable deposit. Additional drilling and sampling may be done to determine the existence of greater quantities of ore for larger scale operations, to determine the limits of the ore zone, for planning of mining techniques and pit design, and for selection of plant sites that will not interfere with the extraction of the ore. Additional factors particularly applicable to the economic evaluation of iron-ore deposits have recently been discussed by Ohle (1972).

PROBLEMS FOR RESEARCH

Specific regions that ought to be studied or reappraised geologically are: (1) Parts of the Adirondack Mountains area of northern New York, for titaniferous and nontitaniferous iron deposits; (2) selected parts of the Lake Superior region, particularly the South Cuyuna Range and adjoining areas, for iron-formation in the subsurface; (3) the Cebolla Creek area, Colorado, for titaniferous deposits; (4) iron-ore districts in southwestern Utah, for magnetite and hematite deposits; (5) iron-ore districts in parts of Nevada, for magnetite and hematite deposits; and (6) the Iliamna Lake area in southwestern Alaska, for titaniferous magnetite deposits. Some of these areas have been reconnoitered or studied in more detail by private investigators, but sufficient data for the appraisal of their iron-ore resource potential are not publicly available. The fact that some areas have been investigated in the past does not eliminate the possibilities for significant discoveries in these areas.

Perhaps the most meaningful studies, from the long-range point of view, would be those directed toward the objective of utilizing the entire iron-rich parts of major iron-formations such as the Biwabik Iron-formation in Minnesota (Dutton, 1955). Such studies would involve sampling, mineralogic investigations, beneficiation tests, and experimentation directed toward new iron-ore smelting techniques. In many places only selected parts of the iron-formation are mined as ore, and large quantities of iron-rich rock must be moved in order to recover the selected parts. For example, the magnetic taconite layer mined may represent only about 150 feet of a total thickness of 500 feet or more of iron-formation. In places, as much as 550 feet of the iron-formation contains more than 23 percent in total iron. Such material would contain about 335 million tons of iron per square mile in a layer 550 feet thick.

The need to minimize environmental problems resulting from mining and processing ores, while assuring adequate domestic supplies of iron ore, gives added incentive to efforts toward use of more

of the total iron in the iron-formation of the Lake Superior region. Processes applicable to utilization of iron in silicates and carbonate as well as in oxides in the Biwabik Iron-formation of the Mesabi Range would be applicable to iron-formations of other districts in the Lake Superior region and elsewhere in the world. If the cost advantage that would be derived from centering more of the nation's production in these large deposits would offset any possible increases in costs of processing the bulk iron-formations, the Lake Superior region could supply much of the nation's expected needs for iron for centuries (Michelson and others, 1970; Roberts and Crago, 1948). Thus, the requirements for land areas for iron mining and associated beneficiation, waste disposal, and transportation facilities would be minimized if more of the iron in the Lake Superior iron-formations were utilized.

The potential iron-ore resources in manganese-iron-rich nodules on the sea floors may be worthy of further investigation because of the possibility that many other valuable products could be extracted from the nodules. These include manganese, copper, nickel, cobalt, zirconium, and titanium. The nodules, however, are probably only of minor potential value for iron.

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KYANITE AND RELATED MINERALS

By Gilbert H. Espenshade

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ABSTRACT OF CONCLUSIONS

Kyanite and related minerals are high-alumina silicates used mainly in the manufacture of refractory linings for metallurgical and other types of furnaces. Domestic production currently exceeds consumption, and considerable tonnages are exported. Enormous resources of these minerals exist in the United States; this should permit the increase in production that will be needed to meet the demand expected during the next 25 years. Production now comes largely from kyanite-quartz deposits in the Southeastern States; kyanite and sillimanite are also recovered as a byproduct from Florida ilmenite sands. Resources of deposits of these two types are very large but make up no more than 5 percent of our total resources. The remaining 95 percent or more is in deposits of micaceous schist and gneiss, mostly in the Appalachian Mountain system and in Idaho. None of these deposits is now being mined, but profitable mining of some may eventually be possible. More detailed geologic studies and sampling of deposits of the kyanite-group minerals are needed in order to appraise their economic potential.

INTRODUCTION

Kyanite and related minerals (known as the kyanite or sillimanite group) are high-alumina minerals used in the manufacture of high-quality refractory materials and other ceramic products. The most abundant are kyanite, sillimanite, and andalusite, all having the same chemical composition, Al_2SiO_5 (also written $Al_2O_3 \cdot SiO_2$), but different physical properties. Dumortierite (containing boron) and topaz (containing fluorine) have similar composition but are much scarcer. Each of these minerals has been produced in the United States, but since 1950, production has been mostly of kyanite, accompanied by small amounts of andalusite and sillimanite. An excellent comprehensive review of the properties, treatment, and industrial uses of these minerals and the geology of the deposits has been given by Varley (1965).

When these minerals are heated to very high temperatures, the new compounds mullite ($3Al_2O_3 \cdot 2SiO_2$) and silica glass are formed. Mullite can also be made from various materials that contain alumina (Al_2O_3) and silica (SiO_2), such as mixtures of alumina, kaolin, and kyanite, alumina and kaolin, bauxite and kaolin, or alumina and silica sand; this product is known as synthetic mullite (Cooper, 1970, p. 1060–1061). Mullite retains its strength and stability at high temperatures for long periods of time and has become very widely used as a refractory material in the metallurgical industry (Foster, 1960; Klinefelter and Cooper, 1961, p. 3–6; Varley, 1965). The refractory properties are improved as the mullite content of the material is increased.

The United States is now the largest producer and consumer of kyanite and synthetic mullite. Domestic demand for kyanite and synthetic mullite in

1968 was estimated at about 120,000 short tons, and exports were about 20,000 tons; total value of the production was about $10.7 million. The demand in 1968 by different industries and the possible demand in the year 2000 (table 61) were estimated by

TABLE 61.—*Estimated United States demand for kyanite and synthetic mullite*

Industry or use	Estimated demand (short tons)		
	1968	2000	
		Low	High
Iron and steel	50,000	125,000	300,000
Nonferrous metals	35,000	130,000	195,000
Boiler furnaces	6,000	25,000	40,000
Glass	17,000	50,000	140,000
Other uses	12,000	40,000	200,000
Total	120,000	380,000	875,000

Cooper (1970, p. 1066–1069).

According to Cooper, the major trend in the use of these materials as refractories in the next 25 years probably will be to replace other types of refractories in metallurgical, glass, and boiler furnaces. Important nonrefractory uses may also be developed, such as the manufacture of aluminum-silicon alloys, floor and wall tile, spinnable mullite fibers, and blown-wool refractory insulations.

Before 1951, the United States imported more kyanite than it produced because the massive ore ("strategic kyanite") from India and Kenya was required as an essential component in making the best high-alumina refractory bricks. The fine-grained kyanite concentrate produced from domestic disseminated ore is more suitable for other purposes. Manufacture of synthetic mullite began in 1951, and its use has practically eliminated the need for imported massive kyanite.

The increased demand expected in the United States for kyanite-group minerals during the next 25 years can be supplied from our very large domestic resources. All domestic production for many years has come from mines in the Southeastern States; production from these mines can be increased, and probably several new mines can be opened at other deposits in the region. The increased demand for kyanite expected in the Western States could probably be met by mining some of the deposits in Idaho, California, or New Mexico. Expansion of synthetic mullite production might require increased imports of bauxite or alumina, but this need would be very small in comparison to the large quantities of bauxite and alumina imported by the aluminum industry. The trend of exports of kyanite and synthetic mullite from the United States over the next 25 years is difficult to forecast because foreign production will doubtless increase, and trade patterns may change considerably.

EXPLOITATION

Domestic mining of the kyanite-group minerals began in the 1920's when kyanite was mined at Baker Mountain, Va., Ogilby, Calif., and Petaca, N. Mex.; andalusite at White Mountain, Calif.; and dumortierite at Oreana, Nev. Other deposits of various types were mined or prospected between 1930 and 1950. Since 1950, nearly all production has come from kyanite-quartz deposits at Baker Mountain and Willis Mountain, Va., Graves Mountain, Ga., and Henry Knob, S.C.; mining at Henry Knob ceased in 1969. Byproduct recovery of kyanite and sillimanite began in 1968 from Florida sands processed for ilmenite and other heavy minerals. Various aspects of domestic mining operations have been discussed by Espenshade and Potter (1960), Foster (1960), Klinefelter and Cooper (1961), and Cooper (1970).

United States production of kyanite has increased steadily since 1940 when it was 4,241 short tons. By 1950, it was about 15,400 short tons, and in 1960, about 33,000 short tons (Varley, 1965, p. 30). Cooper (1970, p. 1066) stated that it was about 100,000 short tons in 1968.

GEOLOGIC ENVIRONMENT

Kyanite, sillimanite, and andalusite are very common in many parts of the world in aluminous metamorphic rocks which have undergone the deformation and increased temperatures that accompany mountain building. Each of the Al_2SiO_5 minerals forms under certain distinctive ranges of temperature and pressure. Kyanite typically forms in schists and gneisses at fairly high temperatures and pressures, under conditions of strong regional or dynamic metamorphism. Andalusite forms at lower pressure and is very common in the hot zones of contact (or thermal) metamorphism surrounding large intrusions of granite or gabbro. Sillimanite forms at higher temperatures during both regional and contact metamorphism. Mullite is a very rare mineral formed naturally at temperatures even higher than sillimanite. Topaz and dumortierite are much less common than the Al_2SiO_5 minerals. They are most abundant in quartzose deposits, some of which appear to be hydrothermally altered volcanic rock.

The Al_2SiO_5 minerals are principally contained in micaceous schists and gneisses which underlie many square miles in some regions. Kyanite and sillimanite are more abundant than andalusite in these deposits. The content of these minerals may be as much as

40 percent, but generally is less than 15 percent. Their distribution may be very irregular because of variable alumina content of the original beds or layers and the subsequent strong deformation of the layered rock. Usually only one of the Al_2SiO_5 minerals is present, but two of them occur together at some places, and all three have been found together at a few places.

Another important but less common type of deposit consists of quartzose rock that contains one or more of the kyanite-group minerals in association with various other aluminous minerals and quartz. These quartzose deposits generally have a higher content of Al_2SiO_5 minerals (commonly more than 20 percent) than do the micaceous schists and gneisses, but they are much smaller in size. Kyanite is usually more abundant in the quartzose deposits than are other minerals of the group.

The kyanite-group minerals also occur in quartz veins and pegmatites but in relatively small amounts. These minerals are very resistant to weathering and erosion and may accumulate in abundance in the soils overlying the source rocks. Subsequently, the Al_2SiO_5 minerals are concentrated in stream and river alluvium; later in the cycle of sediment transport, they may be preserved in beach sands along with other resistant minerals such as quartz, zircon, monazite, staurolite, and the titanium minerals ilmenite and rutile.

RESOURCES

UNITED STATES RESOURCES OF KYANITE-GROUP MINERALS

The Al_2SiO_5 minerals occur in nearly every large area of metamorphic rocks in the country (Espenshade, 1961, 1962; Varley, 1965). The kyanite-group minerals have been found in bedrock at innumerable places in at least 30 States (Grametbauer, 1959). At many places, no more than a few percent of these minerals is contained in the rock, too little to be of economic interest. Only those deposits that contain at least 10 percent of the Al_2SiO_5 minerals are of potential economic value. All domestic resources are of the disseminated type of ore in which the kyanite minerals must be separated from quartz, mica, and other minerals by beneficiation.

Domestic resources of the kyanite-group minerals are summarized in table 62 according to three types of deposits. Enormous amounts of the Al_2SiO_5 minerals are contained in micaceous schists and gneiss, but such deposits typically have lower contents of these minerals than do the quartzose deposits and have produced only a few percent of the total domestic output of these minerals. Probably at least 95 percent of total production has come from quartzose deposits, although these deposits contain no more than 5 percent of our resources.

TABLE 62.—*United States resources of kyanite and related minerals*

[Short tons of contained kyanite-group minerals]

Type of deposit	Resources	
	Identified [1]	Hypothetical [2]
Deposits of micaceous schist and gneiss	950,000,000	1,000,000,000
Quartzose deposits	33,300,000	11,000,000
Byproduct or potential byproduct from deposits mined for other minerals	13,500,000	25,000,000

[1] Identified resources: Specific, identified mineral deposits that may or may not be evaluated as to extent and grade, and whose contained minerals may or may not be profitably recoverable with existing technology and economic conditions.

[2] Hypothetical resources: Undiscovered mineral deposits, whether of recoverable or subeconomic grade, that are geologically predictable as existing in known districts.

The data used in estimating these resources are generally better for the quartzose deposits and byproduct sources than for the deposits of micaceous schist and gneiss. For identified resources, the minimum grade (except for byproduct sources) has been taken as 10 percent content of kyanite-group minerals; estimates of open-cut mining depths range from 50 feet to several hundred feet. Estimates of hypothetical resources are based on extensions of known deposits or districts in depth or in area. None of the micaceous schist and gneiss deposits included in table 62 is now being mined, but profitable mining of some may become possible within the next 25 years. Deposits of sillimanite schist containing finely fibrous sillimanite ("fibrolite") are not included in the resource estimate because of the difficulty in making a clean and efficient separation of this variety of sillimanite.

DEPOSITS OF MICACEOUS SCHIST AND GNEISS

Kyanite and sillimanite are widely distributed in micaceous schist and gneiss in the Appalachian mountain system from Maine to Alabama. Andalusite in such rocks is much more restricted in occurrence and is found principally in New England. General distribution of the Al_2SiO_5 minerals in the Appalachians was shown on a map by Morgan (1972); distribution in New England has also been given (Doll and others, 1961; Hussey and others, 1967; and Thompson and Norton, 1968); distribution in parts of the southern Appalachians was given by Overstreet and others (1968), Carpenter (1970), and Hadley and Nelson (1971). The principal Appalachian deposits of micaceous schist and gneiss included in table 62 are kyanite-garnet-mica gneisses near New Hartford, Conn. (R. W. Schnabel, written commun., Apr. 1972); similar gneiss and

schist near Spruce Pine, N.C. (Brobst, 1962), Clarkesville, Ga., and other areas in the Blue Ridge; andalusite in the contact zones of gabbroic and granitic plutons in central Maine (Espenshade and Boudette, 1967); and sillimanite schist in Hart County, Ga. (Teague, 1950).

The Al_2SiO_5 minerals are also widely distributed in micaceous schist and gneiss in Idaho, Montana, Colorado, the Black Hills, S. Dak., the Sierra Nevada, Calif., and parts of Washington (Thorsen, 1966) and Oregon. However, the only deposits that are large enough and rich enough to be regarded as important resources are the kyanite-sillimanite deposit at Woodrat Mountain and the kyanite-andalusite deposit at Goat Mountain, Idaho (Hietanen, 1956; Van Noy and others, 1970).

QUARTZOSE DEPOSITS

The principal quartzose deposits of kyanite-group minerals are in the southern Piedmont (Hurst, 1959; Espenshade and Potter, 1960). Nearly all domestic kyanite production since 1950 has come from mines at Willis Mountain and Baker Mountain, Va., at Henry Knob in the Kings Mountain district, N.C. and S.C., and at Graves Mountain, Ga. Most resources of quartzose deposits are at these localities and in other kyanite-quartz deposits in the Piedmont. Smaller deposits containing other minerals of the kyanite group that are also included in table 62 are sillimanite-quartz deposits in the Kings Mountain district and some andalusite-pyrophyllite-quartz deposits in North Carolina.

Quartzose deposits of kyanite-group minerals in the Western States are much smaller than those in the Southeastern States. Such deposits are found in New Mexico in the Picuris Range and the Petaca district (Montgomery, 1953; Corey, 1960). An unusual deposit of topaz, sillimanite, and rutile in quartzose gneiss occurs in the Front Range of Colorado (Sheridan and others, 1968). In California, kyanite has been mined from quartzose deposits near Ogilby, Imperial County (Henshaw, 1942), and andalusite has been mined at White Mountain, Mono County (Wright, 1957). Dumortierite and andalusite were once mined from quartzose deposits in altered rhyolite near Oreana, Nev. (Kerr and Jenney, 1935).

BYPRODUCT SOURCES OF KYANITE-GROUP MINERALS

Kyanite and sillimanite occur in small amounts in the sands mined for ilmenite and other heavy minerals in Florida, Georgia, and New Jersey; they have been recovered from the Florida sands since 1968 (Browning and others, 1956; Markewicz, 1969; Cooper, 1970). These minerals are also present in very small amounts along with other heavy minerals in the pebble phosphate deposits of Florida; none of the heavy minerals has been recovered, but Stow (1968) estimated that about 200,000 short tons of heavy minerals (containing about 16 percent kyanite and sillimanite) are discarded yearly from the phosphate mining operations. Topaz occurs in the molybdenum ore at Climax, Colo. (Wallace and others, 1968) and is a potential byproduct.

FOREIGN RESOURCES OF KYANITE-GROUP MINERALS

According to Varley (1965), the minerals of the kyanite group are widely distributed in many countries; the principal deposits of economic value are the quartzose type, as in the United States. Many foreign quartzose deposits contain massive segregations of the Al_2SiO_5 minerals, which in places have accumulated as loose boulders and fragments in the surficial residuum. Such massive ore is easily mined and requires little or no beneficiation, in contrast to domestic disseminated ores.

India has been the principal foreign producer of Al_2SiO_5 minerals since the 1920's, mostly massive kyanite from Lapsa Buru, Singhbhum, Bihar, and massive sillimanite from Assam and Madhya Pradesh. Sillimanite was once recovered from ilmenite beach placers in Kerala and Madras. The Republic of South Africa has also been a major producer for many years, mining andalusite from river placers in the Marico district, Transvaal, and sillimanite-corundum from near Pella, Namaqualand. Kenya was an important producer of both massive kyanite and kyanite concentrates from 1943 to 1960. Massive kyanite has also been produced from South West Africa, Bechuanaland, Rhodesia, and Nyasaland. Sillimanite and small amounts of kyanite and andalusite have been produced in Australia since the 1930's. In the U.S.S.R., andalusite has been produced on a large scale from quartzose deposits in Kazakhstan; important deposits of kyanite occur on the Kola Peninsula and of sillimanite, in eastern Siberia.

Cooper (1970, p. 1062) estimated that foreign reserves amount to 82,500,000 tons, mainly in the U.S.S.R., the Republic of South Africa, Canada, and India. Resources in the sense used here are clearly far larger and must be enormous in the case of the U.S.S.R., India, and some African countries. The data, however, are not adequate for a reliable estimate of foreign resources.

SPECULATIVE RESOURCES

The Al_2SiO_5 minerals are so common in metamorphic rocks that they will be continually discovered as geologic mapping progresses in metamorphic terranes in the United States and other

countries. Probably some of these deposits will be rich enough and large enough to be of potential economic value, but many will be too low in grade for exploitation in the next 25 years. Resources in undiscovered deposits and districts in the United States are doubtless enormous and may exceed our identified and hypothetical resources.

PROBLEMS FOR RESEARCH

The information available about grade and size of many deposits of the kyanite-group minerals is insufficient for meaningful economic appraisals because the economic potential of a deposit is difficult to assess by conventional geologic studies. As the Al_2SiO_5 minerals are highly resistant to weathering and erosion, high-grade rock is commonly better exposed than low-grade rock, and consequently a deposit may appear much richer than it actually is. Detailed mapping and sampling are necessary to determine the extent of high-grade and low-grade rock. A careful preliminary evaluation by these means will be very useful to economic geologists as a guide to deposits which may deserve more exploration.

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LEAD

By H. T. Morris, Allen V. Heyl, and Robert B. Hall

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ABSTRACT OF CONCLUSIONS

Lead has been used by man for approximately 6,000 years; it is now the fifth most important metal of trade in our industrialized economy. Lead occurs in a wide variety of ore deposits that are mined in more than 40 countries on all the continents except Antarctica. The world reserves are here estimated to exceed 140 million short tons of lead contained in ores, equivalent to a 31-year supply at the 1971 world rate of consumption. The reserves of the United States are estimated to constitute 38,185,000 short tons of lead; average annual domestic consumption during the period 1961–70 was 1,240,000 short tons, of which about 43 percent was recycled scrap. The outlook for the continuing discovery of additional reserves and resources at a rate that exceeds consumption is believed to be excellent; many of these undiscovered ore deposits are assumed to be comparable in tonnage and grade with known ore bodies.

Conditional resources of conventional types but low grades are contained in strata-bound, massive sulfide, and other kinds of deposits in several areas of the United States. Conditional resources of unconventional types are contained in lead-bearing manganese nodules on the sea floors, in the Kupferschiefer and related strata of Europe, in the Belt Supergroup of the Northwest United States, and in sediment in thermal deeps of the Red Sea and other oceanic areas. These conditional resources may total as much as 1.5 billion tons of lead, most of which is in the manganese nodules. Hypothetical and speculative resources together may equal half again as much as the known world reserves.

INTRODUCTION

ANCIENT USES

The earliest uses of lead greatly antedate the earliest uses of iron, and lead, with copper and silver, may have been one of the first metals smelted from sulfide or oxidized ores. Because of its relatively common occurrence, the simplicity of its metallurgical reduction, its high density and low fusibility, and its softness and malleability, lead was used by many ancient peoples. As early as 3800 B.C. it was used by an artisan or priest to fashion a figurine that was discovered at the site of the Temple of Osiris at Abydos, in upper Egypt (Mitman, 1922, p. 596). During the succeeding centuries, it

was commonly recovered with silver and used increasingly by the Egyptians, Cretans, Babylonians, and other ancient people in castings, as pottery glaze, as sheets and solder, and as an additive to bronze. In 2000 B.C. the Chinese were using lead coinage, and about the same time the Babylonians were employing soldered lead sheets as roofing for temples and public buildings among other uses. Some of this lead was probably obtained in trade with the Hittites in Asia Minor, who had discovered the technique of smelting iron. By about 1600 B.C., the Phoenicians, who established a farflung commerce in many commodities, had developed lead mines in Cyprus, Greece, Sardinia, and Spain. The ancient Britons bartered lead ores for products of the East brought by the Phoenician seafarers, and this trade was maintained and expanded with the Carthaginians and other seafarers who succeeded them.

Lead was used extensively by the Greeks and Romans. The mines of Laurium, near Athens, among others, supplied the Greeks with silver to finance their wars and with lead for construction of their cities. The segments, or "drums," of the fluted columns that characterize Greek architecture are pinned together by iron rods fitted into sockets that were filled with molten lead. Lead was also used for slip-joint pipes that are remarkably similar to modern soil pipe and was used in coinage, in the production of bronze, and in the arts. Lead compounds were widely used as pigments and cosmetics by both the Romans and the Greeks and in ointments and salves. The Romans extended the mining of argentiferous lead ores into Yugoslavia, Rumania, France, Belgium, and Turkey, chiefly in a search for ever-greater amounts of silver to finance their conquests and enrich Rome. Traces of Roman mining activities are still evident in these countries as well as in Italy, Sardinia, and Spain, where lead objects are occasionally found during the course of modern mining and archaeological activities. In Britain, for example, lead pipes of the Roman era still carry water at the hot-spring area of Bath.

Many of the mines that were originally developed in all of those countries by the Phoenicians and Romans as well as other mines developed in Germany during the Dark Ages after the collapse of the Roman Empire are still important sources of lead in modern world trade and technology.

MODERN USES

In the present industrial economy of the world, lead is the fifth-ranking metal of trade and consumption after iron and steel, aluminum, copper, and zinc. Of the total world mine production in 1969, 3,523,401 short tons (table 63), the United States production was 509,013 short tons, or 14.4 percent. In contrast, the consumption in the United States of lead from all sources, including scrap, was

TABLE 63.—*World mine production of lead in 1969, by countries*

[NA, not available. Data from U.S. Bureau of Mines Minerals Yearbook, 1971]

	Short tons
North America:	
Canada	330,781
Guatemala	[1]314
Honduras	15,255
Mexico	188,378
United States	[1]509,013
South America:	
Argentina	35,000
Bolivia	[e]27,819
Brazil	30,416
Chile	906
Colombia	451
Peru	[1]179,592
Europe:	
Austria	7,500
Bulgaria	[e]90,940
Czechoslovakia	[e]8,000
Finland	5,019
France	[e]33,400
Germany:	
East	[e]13,000
West	43,335
Greece	9,458
Ireland	[e]63,700
Italy	[e]39,700
Norway	[e]3,500
Poland	54,000
Portugal	[e]2,170
Roumania	[e][2]44,000
Spain	76,700
Sweden	[e]79,000
U.S.S.R.	490,000
United Kingdom	[e]3,300
Yugoslavia	135,600
Africa:	
Algeria	[e]7,200
Congo (Brazzaville)	[e]NA
Morocco	77,832
Nigeria	-------
Southwest Africa	[1]66,634
Tunisia	[2e]16,500
Zambia	[2e]25,350
Asia:	
Burma	[e]9,900
China, mainland	[e]110,000
India	2,239
Iran	[e]26,400
Japan	70,037
Korea:	
North	[e]77,000
South	18,163
Philippines	74
Thailand	2,094
Turkey	2,440
Oceania:	
Australia	490,891
Total (listed figures only)	3,523,401

[e] Estimated.
[1] Recoverable.
[2] Smelter production.

1,389,358 short tons, 39.4 percent of the world's primary mine production (table 64).

TABLE 64.—*Lead consumption in the United States, by products, in 1969*

[Data from U.S. Bureau of Mines Minerals Yearbook, 1971]

	Short tons
Metal products:	
Ammunition	79,233
Bearing metals	17,406
Brass and bronze	21,512
Cable covering	54,203
Casting metals	9,918
Caulking lead	44,857
Collapsible tubes	12,484
Foil	5,881
Pipes, traps, and bends	19,407
Sheet lead	25,818
Solder	72,626
Storage batteries:	
Battery grids, posts, etc	280,386
Battery oxides	302,160
Terne metal	1,583
Type metal	25,660
Total	973,134
Pigments:	
White lead	6,617
Red lead and litharge	79,898
Pigment colors	14,670
Other (incl. leaded zinc oxide, etc)	1,201
Total	102,386
Chemicals:	
Gasoline antiknock additive	271,128
Miscellaneous chemicals	602
Total	271,730
Miscellaneous uses:	
Annealing	4,252
Galvanizing	1,797
Lead plating	406
Weights and ballast	17,366
Total	23,821
Other, unclassified uses	18,287
Grand total [1]	1,389,358

[1] Includes lead that went directly from scrap to fabricated products.

The consumption of lead in the United States is dominated by its use in storage batteries and leaded gasoline and in the construction industry, as shown in table 64. Other important but apparently diminishing uses are in pigments, cable sheathing, type metal, and ammunition. It is significant to note, however, that only the lead used in paint pigments and ammunition and in tetraethyl lead fluids and other chemical compounds is nonrecoverable. Much of the lead used for other purposes, particularly as grids in storage batteries, is recyclable and eventually returns to the market in the form of scrap.

From 1951 to 1971, the consumption of lead in the United States increased from 1,185,000 short tons to 1,380,000 short tons, an increase of 16.5 percent, whereas increase in world consumption, from approximately 2,170,000 short tons to approximately 4,563,000 short tons, was 110 percent (U.S. Bur. Mines unpub. data, 1972). The burgeoning world consumption of lead as compared with United States consumption is attributed to the expanding use of passenger automobiles, trucks, and other modes of transportation and to the growth of the communications industry throughout the world, especially in Europe and Japan.

OUTLOOK

According to the U.S. Bureau of Mines survey (Paone, 1970, p. 615), projection of population growth statistics, consumption data, and other factors to the year 2000 indicate a continuing increase in the United States demand for lead in the production of storage batteries, leaded gasoline, bearings, and possibly in the construction industry; in contrast, only moderate to small increases are forecast for the use of lead in small-arms ammunition, insecticides, packaging, and radiation shields, and decreases are anticipated in the printing industry and in the manufacture of paint pigments. As noted by Paone (1970, p. 615), the U.S. demand for lead for storage batteries and leaded gasoline may be expected to triple or quadruple during the next 30 years, whereas the demand for other uses is expected to show only a fractional increase or an actual decrease. The current antipollution standards, if rigorously applied during this interval, undoubtedly will substantially modify the projected increase for leaded gasoline through the greater use of diesel engines, gas turbines, and electric vehicles and by the continued development of low-lead or lead-free high-octane gasolines. Similarly, the successful development of lightweight sodium-sulfur and lithium- or sodium-water batteries may substantially diminish the demand for the heavier, lead-acid batteries despite the expected increase in the total number of accessorized automobiles and trucks and electric vehicles by the year 2000.

All things considered, the large domestic resources of lead appear to be adequate to supply an increasingly larger proportion of the needs of the United States, at least to the year 2000, despite the rapidly expanding consumption of the rest of the world.

EXPLOITATION

Production of primary lead in the world and in the United States and the United States consumption of lead from all sources are summarized in figure 39. It is estimated, in part using data presented by Smith (1929), that world production from prehistoric time to 1969 was about 151,162,000

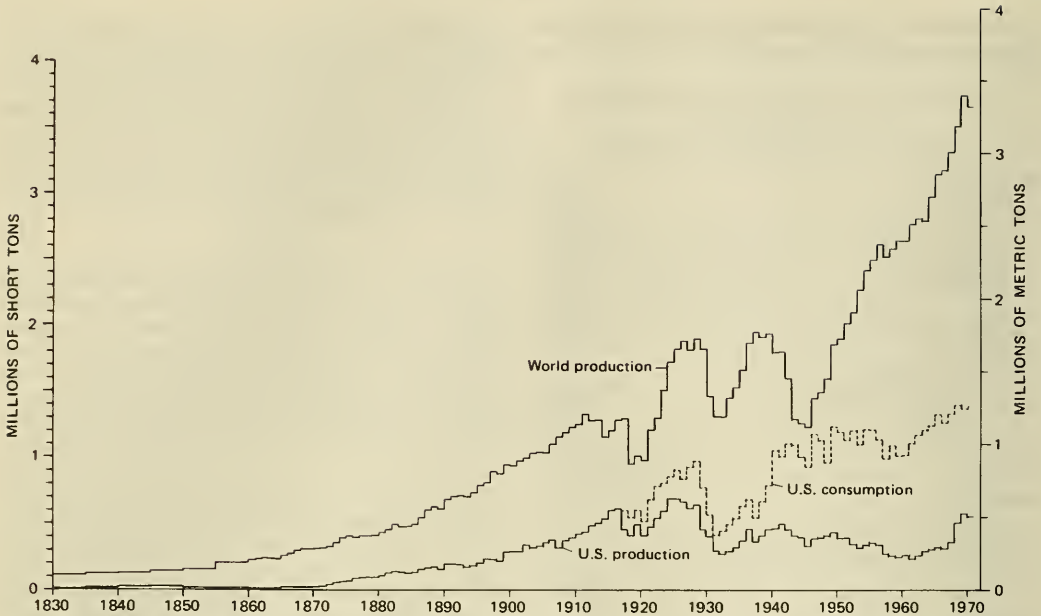

FIGURE 39.—Production of primary lead in the world and in the United States, 1830–1971, and consumption of lead, including scrap, in the United States, 1918–71. Data from U.S. Geological Survey, U.S. Bureau of Mines, and American Bureau of Metal Statistics.

short tons. Of this amount, less than 5 million tons is estimated to have been produced prior to 1800, 25,167,000 tons from 1801 to 1900, and 120,995,000 tons from 1901 to 1969. Production during the next decade will certainly exceed the production of the entire 19th century.

The significant variations in the production curves of lead for both the United States and the world are largely related to political and economic factors rather than to the discovery of large ore deposits or to technological advancements in mining, milling, or smelting. The effects of major events on world production of lead include: (1) a leveling of production during World War I, (2) a small decline during the postwar economic recession of 1919–21 followed by a steep rise in production, (3) a second decline during the depression years of the early 1930's, also followed by a steep rise, and (4) a third major decline, essentially coincident with World War II, followed by a rise in production that has been relatively unbroken since 1946. The United States production through 1940 in general shows the same perturbations as the world production but differs in some respects. During the period 1916–18, a slight increase in production reflects increased U.S. exports, presumably to the warring nations of western Europe. The decade of prosperity between the economic recessions of 1920 and 1930 did not result in a rise in U.S. production comparable in magnitude to the rise in world production; during this interval the United States became a significant importer of lead. After the depression years of the 1930's our highest domestic production was one-third less than in the best predepression years, and production generally declined from 1942 to 1962, largely as a result of depletion of many of our major deposits. Since 1962, approximately the time of the first production from the new mines in the Viburnum area of southeast Missouri, U.S. production has increased; by 1970 it had reached 572,000 tons.

The current and future discovery and exploitation of lead deposits throughout the world will undoubtedly continue to be controlled more by economic, political, and environmental considerations than by technological advances. In recent decades such advances have more than offset the losses in production resulting from the exhaustion of many small

high-grade deposits, particularly those that produced lead as a coproduct with silver and other metals. These advances include the development of high-volume mining and milling techniques that have allowed the profitable exploitation of large low-grade disseminated ore bodies; the successful application of new techniques of continuous smelting of intimately mixed zinc and lead ores; the recovery of byproduct lead concentrate from the milling of massive sulfide ores in Sweden, Japan, and elsewhere; and, most importantly, the continued discovery and development of conventional types of ore bodies. Certain trends, however, tend to indicate a softening demand for lead in the future, particularly in the United States and Western Europe. These trends include severe limitations on the permissible levels of sulfur dioxide, lead oxide, and other emissions from smelters; significant reductions in the lead content of high-octane gasoline; the virtual elimination of lead oxides in paint; and the substitution of other substances for the lead used in cable sheathing, type metal, and other applications. Whether or not increased consumption of lead in some uses (such as batteries) will offset declining consumption in other uses (such as tetraethyl lead gasoline additive) over the near term is difficult to predict. It seems certain, however, that world production and consumption of newly mined lead will increase over the long term, but eventually must decline as the primary sources approach exhaustion and the recycling of scrap lead increases.

GEOLOGIC ENVIRONMENT

GEOCHEMISTRY

Lead is a chemical element of atomic number 82. The atomic weight varies because of variations in isotope composition which are due to unequal incorporation of radiogenic lead, the product of atomic decomposition of both uranium and thorium. Common lead of isotopic composition Pb^{204} 1.5 percent, Pb^{206} 23.6 percent, Pb^{207} 22.6 percent, and Pb^{208} 52.3 percent has an atomic weight of 207.2. Lead occurs in nature rarely as the metallic element and in the quadrivalent state but predominantly in the divalent state with an ionic radius of 1.26 A for sixfold coordination. Commonly it diadochically replaces Ba^{+2} (1.44 A), Sr^{+2} (1.21 A), and K^{+1} (1.46 A) in the lattice of certain silicates, phosphates, and other minerals.

Lead is the 34th most abundant element in the lithosphere, averaging about 15 ppm (parts per million). In crustal abundance, it ranks not only below copper and zinc but also below such less common and even rare elements as yttrium, neodymium, lanthanum, and possibly gallium (Mason, 1958, p. 44). In igneous rocks it ranges in concentration from approximately 5 ppm in gabbro and related rocks to 10 ppm in oceanic crust and approximately 20 ppm in granite. Typical concentrations in sedimentary rocks range from an average of 7 ppm in sandstone and 9 ppm in carbonate rocks to 20 ppm in shales; deep-sea clays reportedly average 80 ppm (Turekian and Wedepohl, 1961, table 2). Inasmuch as lead ores of minimum minable grade average about 4 percent, they represent a concentration factor of 2,600 times the average crustal composition, or about 2,000 times the average concentration in granite.

Lead appears to be chiefly siderophile, according to Rankama and Sahama (1950, p. 729–730), although it may also be chalcophile; in the lithosphere it shows a rather pronounced affinity for sulfur and also for oxygen. Lead is essentially absent as an early magmatic sulfide and is particularly enriched in pneumatolytic and hydrothermal solutions genetically associated with quartz-bearing igneous rocks. It is the major constituent of more than 200 known minerals.

In primary ore deposits, lead occurs predominantly as the sulfide. During weathering, this sulfide is slowly oxidized to lead sulfate, a process that is facilitated by the concurrent oxidation of the commonly associated pyrite to ferric sulfate, which acts as an oxidizing agent. The lead sulfate, which is only moderately soluble, and therefore relatively stable, is in turn converted by the action of carbon dioxide or soluble bicarbonates to the even more stable lead carbonate, which is the most chemically resistant lead compound in the zone of oxidation. Other rarer compounds that may be formed in the oxidation zone include arsenates, chlorides, vanadates, phosphates, chromates, and molybdates. In time even the stable lead carbonate is physically disaggregated or is taken into solution as the moderately soluble lead bicarbonate and finds its way to the sea.

ORE MINERALOGY

In the wide variety of lead-producing deposits throughout the world, the overwhelmingly dominant ore mineral is galena (PbS). This metallic, steel-gray mineral with perfect cubic cleavage is one of the most widely distributed and easily recognized ore minerals. Very commonly it contains silver, usually as occluded blebs of argentite (Ag_2S), argentiferous tetrahedrite ($3[Cu \cdot Ag]_2S \cdot Sb_2S_3$), and similar minerals; it becomes silver ore when the value of silver exceeds that of the contained lead. Near the surface,

many of the galena ore bodies are altered to cerussite ($PbCO_3$), anglesite ($PbSO_4$), pyromorphite ($Pb_4[PbCl][PO_4]_3$), and other minerals, but commercial ores consisting chiefly of these secondary minerals now represent only a small fraction of the total volume of lead ores currently being produced. A great many other metallic lead minerals have been recognized, including many silver-, copper-, bismuth-, and antimony-bearing sulfosalts that are important sources of silver and other metals. Only rarely are these minerals found in concentrations large enough to produce a significant quantity of lead.

The primary metallic minerals most commonly associated with galena include pyrite (FeS_2), sphalerite (ZnS), chalcopyrite ($CuFeS_2$), tetrahedrite ($3Cu_2S \cdot Sb_2S_3$) or tennantite ($3Cu_2S \cdot As_2S_3$), argentite, bournonite ($3PbS \cdot Cu_2S \cdot Sb_2S_3$), and other sulfosalts, and, locally, marcasite (FeS_2) and pyrrhotite (Fe_7S_8). Sphalerite, in particular, is such a common associate of galena that sphalerite-free galena ore bodies and galena-free sphalerite ore bodies are rare. The primary gangue minerals found in lead deposits include quartz in various forms; calcite, dolomite, and other carbonates; barite; and fluorite. Some of these minerals, as well as many of the associated minor metallic minerals, commonly are recovered as coproducts and byproducts.

TYPES OF DEPOSITS

The ore bodies in which galena is a major or a recoverable minor constituent have been deposited in a wide variety of physical and chemical environments. They are most effectively classified on the basis of their geologic occurrence as: (1) strata-bound deposits of syngenetic origin, (2) strata-bound or stratiform deposits of epigenetic origin, (3) volcano-sedimentary deposits and their metamorphic equivalents, (4) replacement deposits, including mantos, (5) veins, and (6) contact pyrometasomatic deposits in the aureoles of granitic plutons. As with other types of classification systems, the above scheme is not wholly satisfactory, inasmuch as one type of deposit—such as a vein—may gradually assume the characteristics of another type—such as a replacement deposit. Also, there is much disagreement among geologists and geochemists as to the genesis of many ore bodies, particularly the strata-bound deposits, which may have either a syngenetic or an epigenetic origin. As pointed out by Brown (1970, p. 108), it is remarkable that so many well-qualified authorities can examine the same set of facts about the strata-bound ore bodies and reach such widely different conclusions as to their genesis. In recent years, however, studies of fluid inclusions and of lead, sulfur, and oxygen isotopes and their ratios in various deposits of unquestioned origin appear to have helped resolve questions of the origin of some previously enigmatic ore bodies. (NOTE.—Usage of the terms "strata-bound" and "stratiform" in this chapter is somewhat different from usage in some other chapters.)

STRATA-BOUND DEPOSITS OF SYNGENETIC ORIGIN

The largest and most productive lead deposits are those that are apparently restricted to one or more sedimentary rock units, chiefly limestone, dolomite, or shale. Many of these deposits underlie areas exceeding several square kilometers and are, in fact, merely the richer parts of broadly mineralized terranes that extend for many hundreds or even thousands of square kilometers. Detailed studies commonly reveal that these deposits may be further divided into two general types: those in which the ore minerals were deposited syngenetically with the enclosing sediments or formed shortly afterward as a result of diagenetic processes and those in which the ore minerals chiefly occur in secondary features and commonly are enclosed within aureoles of secondary dolomitization or some other form of post-diagenetic alteration. Although deposits of the latter type have many features in common with the replacement deposits, particularly the mantos, they generally differ in the absence of any clear evidence of their association with igneous rocks. These epigenetic deposits are discussed separately.

The strata-bound ores of syngenetic origin are typified by the "Kupferschiefer" bed, near the base of the Zechstein Formation, which is currently being mined in East Germany in the area of Mansfeld, Richelsdorf, and Sangerhausen and in Poland in the Subsudetic syncline. This layer of bituminous shale is commonly 1 meter or less thick; it locally overlies a patchy marine conglomerate, the first stratum deposited in the Upper Permian basin of central Germany, and underlies a sequence containing limestone, gypsum, halite, and sandstone. It is reportedly mineralized over an area of 4,560 square kilometers (Bauchau, 1971, p. 5). The ore minerals are finely disseminated through the shale and consist predominantly of bornite, chalcocite, galena, sphalerite, and tetrahedrite. Accessory elements include nickel, cobalt, selenium, vanadium, molybdenum, and silver. There are virtually no gangue minerals except for wispy veinlets of barite and gypsum. Here and there the Kupferschiefer is cut by small faults, and near them the bed may be either enriched or impoverished in the metals; locally, some of these faults contain

secondary ore minerals and have been mined as lodes.

The general grade of the Kupferschiefer bed that has been mined for its copper content is 2–3 percent copper, 1.3 percent zinc, about 1.5 percent lead, and approximately 4 ounces per short ton silver. Elsewhere, the content of zinc and lead is higher, as at Uftrungen, where the bed averages 2.5 percent lead and 1.7 percent zinc (Deans, 1950, p. 343). Overall, the Kupferschiefer may contain an average zinc and lead concentration more than 10 times higher than that of copper (Wedepohl, 1971, p. 269).

The genesis of the Kupferschiefer has been the subject of much controversy. Most geologists who have studied the deposits favor a syngenetic origin because of the virtual restriction of the ore minerals to a thin stratum that is rich in organic carbon, the fine dissemination of the ore minerals, the apparent bacterial origin of the contained sulfur, the patterns of both vertical and regional zonation of the ore metals, and the wide occurrence of ore minerals in correlative units in western Poland, western Germany, and northeast England. According to Richter-Bernburg (1941), however, the metals occur in the Kupferschiefer in such great volume that they could not have been derived entirely from the denudation of ore deposits in the surrounding landmasses during the short time available for deposition of the thin ore bed. He suggested that they were enriched over a long period of time in deep-lying ground water, which later rose to mingle with the early Zechstein sea. Wedepohl (1971), in a more recent study, favored the gradual deposition of metals in the anoxic bottom waters of the Kupferschiefer sea as it transgressed over a peneplane cut into red-bed country rocks. He further stated that time factors and the occurrence of the main ore-bearing zones at the margins of the Kupferschiefer sea virtually rule out an origin from submarine springs of cryptovolcanic affinity.

Although other possibly syngenetic strata-bound deposits of copper are not uncommon, particularly in south-central Africa, lead-bearing deposits of unquestioned syngenetic origin are rare. Strata-bound deposits of lead minerals in the Precambrian Belt Supergroup of northern Idaho and northwestern Montana have recently been described by Clark (1971). In this area, the somewhat better explored strata-bound copper deposits—whose origin is still in debate (see "Copper" chapter)—are locally overlain by zones of galena-impregnated rock that contain as much as 6 percent of lead. Unlike the Kupferschiefer, the host rocks are most commonly carbonate-rich quartzite and siltite, and zinc minerals are rare to absent. Deposits that are closely similar to the separated strata-bound copper and lead deposits of the Belt Supergroup have been described at Dzhezkazgan in central Kazakhstan by Shcherba (1971, p. 173–174). It should also be noted that many strata-bound deposits in Europe and northern Africa, considered by European geologists to be syngenetic, have many of the characteristics of the stratiform epigenetic deposits described in the following section. (See Brown, 1970.)

STRATA-BOUND DEPOSITS OF EPIGENETIC ORIGIN

Ore deposits that are essentially restricted to one or a few well-defined tabular stratigraphic units, chiefly limestone or dolomite, but which are clearly younger than the lithification of the host rocks and are not obviously related to any igneous rocks, account for most of the lead that has been produced in the world or is known as reserves (Bauchau, 1971, p. 9). For some of these deposits, the widely used term "strata-bound" may be misleading. As noted by Brown (1970, p. 104), the ores occur mainly in certain preferred horizons or strata, and most are sufficiently conformable to bedding to be described as stratiform; as the ore bodies commonly occur in several formations of different ages, however, they also may be closely related to cross-breaking fractures, breccia pipes, and other tectonic features.

In general, the most common host rocks of the epigenetic stratiform deposits are shallow-water marine carbonate rocks. In many areas they are most heavily mineralized near the rims of the sedimentary basins, adjacent to domelike positive areas, at facies contacts within the basins, or near unconformities within the basin strata. The minerals of the deposits consist predominantly of galena, sphalerite, and pyrite or marcasite. In some mines chalcopyrite, siegenite ($[Co,Ni]_3S_4$), and other sulfides are present, and nickel, cobalt, and copper, as well as cadmium, silver, and germanium, are recovered as byproduct metals. In many deposits, the ore consists predominantly of either galena or sphalerite. In some deposits in the Kentucky-Illinois, central Kentucky, and central Tennessee districts, barite or fluorite are major coproduct constituents, but elsewhere the gangue minerals commonly include only calcite, dolomite, and jasperoid.

The epigenetic stratiform deposits are typically flat lying, although in central Kazakhstan and elsewhere subsequent tectonic activity may have compressed some of them into folds or tilted them steeply within fault blocks. The ore bodies are characteristically large and commonly are localized by stratigraphic pinch-out zones, by masses of breccia of diverse origin, by zones of minor faults and frac-

tures, or by bioherms and associated sedimentary and organic features. Typically, ore does not occur on faults of large displacement, although it commonly occurs adjacent to them. The prevalent occurrence of the ore bodies in carbonate rocks is probably related to the tendency of these rocks to fracture readily and to produce breccias, to develop zones of secondary porosity and even karst environments during periods of preore ground-water movement, and to be highly soluble and reactive. Many individual ore bodies form runs of ore that are several hundred feet wide and 100–200 feet high and have been followed for a mile or more, each containing several million tons of ore. In the Southeast Missouri lead district the average grade of ore in the epigenetic stratiform deposits is 3–8 percent lead, 0.5–1 percent zinc, and 0.10 percent copper; nickel, cobalt, cadmium, silver, germanium, and indium are present in minor amounts. In northeastern Morocco, similar deposits contain 5–7 percent lead in the form of galena and also contain sphalerite, chalcopyrite, and secondary dolomite.

A few of the larger and better known districts containing strata-bound deposits of epigenetic origin include the Southeast Missouri (Snyder and Gerdemann, 1968), Tri-State (McKnight and Fischer, 1970; Brockie and others, 1968), Upper Mississippi Valley (Heyl, 1968), and Metaline (Dings and Whitebread, 1965) districts in the United States, the Pine Point deposit in Canada (Campbell, 1967), Laisvall in Sweden (Grip, 1950, p. 367–369), Mechernich-Maubach and other districts in West Germany (Behrend, 1950), Silesia-Cracow in Poland (Galkiewicz, 1967; Gruszczyk, 1967), Touissit-Bou Beker and other areas in Morocco (Agard, 1967; Jouravsky and others, 1950), and Mirgalimsai, Kazakhstan (Shcherba, 1971, p. 173). Other countries that contain epigenetic strata-bound lead deposits include Spain, France, Belgium, Austria, Italy, and Tunisia. Similar districts here believed to have emerging and potential importance as lead-producing areas in the United States include the Kentucky-Illinois and central Kentucky districts and the recently discovered central Tennessee district. Older districts of the same general type that may continue to be important sources of lead include the Alpine lead-zinc deposits of Europe and the lead and zinc deposits of the Appalachian Valley of the Eastern United States.

Continuing detailed studies of the epigenetic stratiform deposits throughout the world indicate that although these deposits are similar in size and geological character, they differ in important geochemical details. In general, they may be divided into three types: (1) the Upper Mississippi Valley type, (2) the Alpine type, and (3) the stratiform or strata-bound deposits of normal replacement origin. The Mississippi Valley type deposits are named from the extensive lead and zinc ore bodies in the Tri-State, Southeast Missouri, Upper Mississippi Valley, and other districts in the Central United States but are also recognized in Europe and elsewhere. As stressed by Brown (1970, p. 116–117), they are characterized by isotopically anomalous lead of the J-type, which contains an excess of the three radiogenic components Pb^{206}, Pb^{207}, and Pb^{208}, indicating a "future" age. In ore bodies from which an appreciable number of analyses are available, the J-type lead has a fairly wide range in its isotopic character, indicating that the solutions from which it was deposited were not magmatic in origin. Isotopic analyses of the sulfur in the Mississippi Valley type deposits show that it is within the range of sulfur of biogenic origin, the sulfur of connate brines, and normal depositional sulfides in sedimentary rocks.

Studies of fluid inclusions in the sulfide and gangue minerals of the Mississippi Valley type ore bodies suggest that they were deposited from metal-rich brines of moderate salinity at temperatures of 70°–150°C. These brines are of the Na–Ca–Cl type—about five to 10 times as concentrated as sea water—and closely resemble the connate waters found in oil fields in adjacent sedimentary basins. The source of the metals is unknown; the sources favored by most geologists who have worked in the Mississippi Valley districts are the rocks and saline deposits of the sedimentary basins or, in particular, the igneous and metamorphic rocks of the crystalline basement beneath the ore-bearing strata. The tendency for many of the deposits to be localized in stratigraphic traps on the flanks of broad domes suggests that during a period of minor tectonic deformation, connate brines containing metals and other components of the ore bodies that had been leached from adjacent rocks migrated upward along new and preexisting conduits. Ore deposition then followed as a result of chemical and physical changes in the brines when they reached the sites of ore deposition.

The Alpine lead deposits are similar in many respects to the Mississippi Valley type deposits but differ from them in containing B-type lead, whose isotope composition indicates an age older than that of the rocks and structures that enclose the ore bodies. As noted by Brown (1965, p. 65), the isotope composition of the lead in a large number of stratiform deposits in central Europe indicates an essentially uniform Devonian age, although the ore bodies occur in strata ranging in age from Devonian to Triassic. Such leads may have been carried by connate

fluids that percolated through the older Paleozoic strata and later were mixed with a minor proportion of younger lead derived from the host rocks or the prevailing oceans at the date of deposition (Brown, 1970, p. 109). The specific origin of the metals in these deposits and their environment of deposition are the subject of much vigorous debate among European geologists, some of whom favor a syngenetic or a meteoric origin for the deposits.

Strata-bound or stratiform deposits that closely resemble the Mississippi Valley- and Alpine-type deposits but contain lead whose apparent isotopic age is the same as the apparent age of ore deposition, constitute the third class of strata-bound epigenetic deposits. These ore bodies are genetically similar to the vein and replacement deposits described in the following sections. An example of such a deposit is Pine Point in Canada, which contains lead from a homogeneous source with model age of about 250–275 million years, appreciably younger than the Devonian host rocks (Cumming and Robertson, 1969). Additional examples may be found among the Appalachian Valley lead and zinc deposits of east Tennessee, Virginia, and Pennsylvania and in other stratiform deposits in other parts of the world.

VOLCANO-SEDIMENTARY DEPOSITS

The second most productive deposits of lead and zinc are lenticular bodies of massive sulfides that are conformable or semiconformable with interstratified volcanic, volcano-sedimentary, and sedimentary rocks. These deposits range from the relatively little deformed Kuroko deposits of Miocene age in Japan to the recrystallized massive deposits of Paleozoic and Precambrian ages in metamorphic rocks in other parts of the world. Some of these latter deposits form the largest individual concentrations of metal sulfides yet discovered.

The unmetamorphosed volcano-sedimentary, or Kuroko, deposits of Japan are massive pods and lenses of various sizes composed of intimate mixtures of sphalerite, galena, some chalcopyrite, accessory sulfosalt minerals, barite, and gypsum (Kinoshita, 1931; Horikoshi, 1969). Byproducts of gold, silver, tin, tungsten, arsenic, barite, and other elements are recovered locally. The deposits occur chiefly in shale, sandstone, green tuff, and other clastic volcano-sedimentary rocks of Miocene age. Many show a zonal arrangement with lead- and zinc-rich ore (kuroko) in the center, chalcopyrite- and pyrite-rich ore (oko) forming an intermediate zone, and silica-rich pyrite ore (kieko) forming an irregular outer zone next to gypsum-rich altered country rock (Japan Geol. Survey, 1960, p. 141). The deposits are essentially parallel to the stratification of the enclosing volcano-sedimentary rocks, but many are obviously replacement deposits and are surrounded by envelopes of altered rocks. One of the larger ore bodies, the Matsumine, is more than 1,000 meters long, 500 meters wide, and 30 meters thick and originally contained 30,000,000 metric tons of ore. The grade of this ore body is estimated to be 2–2.5 percent copper, 1 percent lead, 3.5 percent zinc, and 17–24 percent sulfur (Maruyama and Sato, 1970, p. 177). Other minable Kuroko deposits range downward in size to the Suehiro ore body, 50 meters long, 40 meters wide, and 30 meters thick, which contains about 40,000 metric tons of ore that averages 4.7 percent copper, 1.7 percent lead, 3.8 percent zinc, and 20.2 percent sulfur (Maruyama and Sato, 1970, p. 177). Some parts of many Kuroko ore bodies, however, consist essentially of massive galena and marmatitic sphalerite.

Geologic and mineralogic relations indicate that the Kuroko ore bodies were formed by submarine exhalative processes during the geosynclinal accumulation of their country rocks. They are most commonly found as replacements of water-laid tuffs and similar rocks beneath caprocks of lava on the flanks of domes that are cored by rhyolite intrusions. Some of the deposits merge downward with veins and stockworks that may represent the conduits for the relatively low temperature mineralizing solutions that formed the massive ore bodies.

Deposits somewhat similar to the Kuroko deposits have been described at Atasu and Achisai in Kazakhstan by Shcherba (1971, p. 172–174).

Massive sulfide deposits in metamorphic rocks have many features in common with the Kuroko deposits including large size, common association with volcanic rocks, strata-bound or stratiform character, simple mineralogy with abundant iron sulfide, and an absence of obvious structural localization. Some of them differ from the Kuroko deposits in containing somewhat higher concentrations of lead and zinc, and in being somewhat coarser textured; both features may be attributable to recrystallization during metamorphism. It is possible that many of these deposits are large replacement bodies that were emplaced long after lithification, uplift, and even metamorphism of the country rock. However, a submarine-exhalative origin is suggested by their apparent concordant nature, their independence from faults and other structural features, and the common absence of nearby intrusive bodies.

As a group, the massive sulfide deposits in metamorphic rocks range in size from small pods containing only a few tons or less to enormous bodies con-

taining more than 100 million tons. The ore is commonly fine grained, consisting of intimate aggregates of pyrite or pyrrhotite, sphalerite, galena, and chalcopyrite, with minor or subordinate amounts of quartz, sericite, chlorite minerals, ankerite, and other carbonate minerals. Host rocks include argillite, metavolcanic rocks, schists of various mineral associations, shale, and carbonate rocks. In folded terranes, the ore bodies are typically, but not invariably, found on the limbs of folds. In such widely separated places as Bathurst, New Brunswick, Jerome, Ariz., and Broken Hill, New South Wales, the ore bodies are intimately associated with metamorphosed quartz porphyry.

As typified by the Bathurst deposits, individual ore lenses may be 3,000 feet or more long and as much as 250 feet wide and may extend to depths greater than 1,700 feet. Zones of en echelon ore lenses in the Bathurst area are nearly a mile long (Gates, 1971, p. 113). The grade of the larger concentrations of lead and zinc ores in the irregularly zoned Brunswick and Heath Steele ore bodies is close to 3–3.5 percent lead and 8.75 percent zinc; copper, silver, and gold are also recovered. Additional examples of volcano-sedimentary deposits in metamorphic rocks include numerous mines in Norway (Vokes, 1962), Sweden (Kautsky, 1957), U.S.S.R. (Smirnow, 1960), especially Leninogorsk and adjacent areas (Nekhoroshev, 1941), and elsewhere (Anderson, 1969). Other great massive ore deposits of the world, such as Mount Isa and Broken Hill in Australia, Rammelsberg and Meggen in West Germany, Kidd Creek and Sullivan in Canada, and Ducktown in the United States, may have originated as volcano-sedimentary deposits, but conclusive evidence of their origin has not been established or may have been obliterated by metamorphism, recrystallization, or subsequent tectonism.

REPLACEMENT DEPOSITS

The third most productive source of primary lead is hydrothermal replacement ore deposits that are commonly associated with postorogenic intrusions of intermediate to acid composition. Most commonly these deposits occur in such readily soluble rocks as limestone and dolomite, but they also occur in quartzite and shale and in igneous and metamorphic rocks. They range in size from insignificant pods to extensive masses like the Cerro de Pasco ore body in Peru, which may have originally contained more than 2.3 million tons of galena, 6 million tons of sphalerite, and 100 million tons of pyrite, and significant amounts of other hydrothermal minerals (recalculated from Peterson, 1965, p. 446). In most of the replacement deposits the dominant lead mineral is galena, which is associated with sphalerite, chalcopyrite, and pyrite. In many deposits, silver, arsenic, antimony, and cadmium are also abundant, giving rise to a great variety of arsenides, antimonides, and sulfosalts. Oxidation, which locally extends to considerable depth, results in a still greater variety of minerals and commonly aids in the enrichment of some lead ore by the solution and migration of more soluble constituents.

The form and size of replacement ore bodies are largely determined by the chemical character of their host rocks and the geologic structures that localize the deposits. In less readily soluble igneous and metamorphic rocks and in quartzite and other refractory sedimentary rocks, replacement deposits commonly assume, wholly or partly, the form of such structural features as tabular fault and shear zones, pipe-shaped masses of intrusion breccia, flat-lying beds or layers of porous tuff, agglomerate, and similar rocks, or podlike masses of breccia of diverse origin. In the more soluble carbonate rocks, the replacement deposits similarly assume the general character of the localizing structural or stratigraphic feature, but they also typically extend irregularly and unpredictably along a variety of minor or obscure features, producing ore bodies that are highly irregular and branching. In gently dipping, relatively unfractured carbonate rocks, particularly in central Mexico and central Colorado, the replacement bodies form flat-lying tabular bodies and near-horizontal pipelike bodies—both called mantos; these bodies commonly extend outward along one or more selected horizons from vertical columns or chimneys of ore that are several hundred feet high, which may or may not be localized by recognizable fractures (Prescott, 1926). Most of the important replacement deposits contain a few hundred thousand to a few million tons of ore. Many of them are small, but some exceed 100 million tons. The grade is commonly of the order of 10–30 percent of lead and zinc combined, 3–5 percent copper, 5–50 ounces per ton silver, and a few hundredths of an ounce of gold per ton. Some deposits show a pronounced vertical or lateral zonation of the metals.

Examples of some of the more important massive replacement ore deposits include Tintic, Utah (Morris, 1968), Bingham, Utah (Rubright and Hart, 1968), Gilman, Colo. (Tweto and Lovering, 1947), Leadville, Colo. (Emmons and others, 1927; Tweto, 1968), central Mexico (Prescott, 1926), central Peru (Peterson, 1965), Sardinia, Italy (Novarese, 1950), Trepča, Yugoslavia (Forgan, 1950), Cartagena, Spain (Pavillon, 1969), Tsumeb, South West

Africa (Tsumeb Corp. Ltd., 1961), Turlan, U.S.S.R. (Knyazev, 1954), and many others. Deposits of doubtful replacement origin include the Broken Hill, Mount Isa, and Hilton ore deposits in Australia, the Sullivan ore body in Canada, and one or more of the massive sulfide deposits in the metamorphic terranes of Scandinavia.

The environments of deposition of hydrothermal replacement deposits range from high pressures and essentially magmatic temperatures to low temperatures and a few atmospheres of pressure. Studies of fluid inclusions, isotopic ratios, and the stability fields of minerals and mineral associations indicate that the highly productive limestone replacement ore bodies were deposited from brines of moderate density at temperatures ranging from 175°C to 500°C and at pressures of 140 to 400 atmospheres. Commonly the terminal phases of ore deposition show relatively low temperatures. Prospecting for these ore bodies in areas where they are entirely concealed is often expensive, frustrating, and unrewarding.

VEINS

Tabular or sheetlike masses of ores that occupy a fracture or sets of fractures are perhaps the most widespread and best known type of ore deposit. In past centuries they have been the principal source of lead ores, and today they are the chief type of deposit being mined in several highly productive mining districts, including the famous Coeur d'Alene district of Idaho. Veins are found in all types of rocks, assuming all possible attitudes and directions. The simplest veins are those in which the ore and gangue minerals partly or wholly occupy the original open spaces along a fracture. Filled veins completely occupy a fracture, commonly leaving no residual masses of country rock; many of them are banded, and some show evidence of rebrecciation and renewal of ore deposition. Replacement veins, which generally occur in limestone and other reactive rocks, so extensively replace their walls that the character of the localizing fracture is commonly obliterated and the veins become indistinguishable from massive replacement deposits. In most districts, veins occur in groups or systems of subparallel trend, in which individual veins branch and divide, commonly joining with adjacent veins by means of diagonal structures. They range in width from narrow seams to exceptional deposits that are 50 feet or more wide. Networks of narrow, short veins, or close-spaced "horsetail" vein systems locally are mined as stockworks or compound lodes. Persistent veins follow faults of moderate to large displacement; in the Harz Mountains, Germany, some of the lead-bearing veins are traceable for 12 miles, and in the Silverton area, Colorado, single ore-bearing fissures are 5 miles or more in length (Lindgren, 1933, p. 164). The vertical extent of most veins is generally less than their length. Some disappear within a few tens of feet below the surface; others have been followed downdip for as much as 10,000–11,000 feet. Because of greatly increased operating costs at depth and the relatively small volume of ore in most ore shoots, only those base-metal veins with a high proportion of gold or silver can be mined below 2,000–3,000 feet.

Few veins contain ore of minable grade for their entire length or depth. The ore minerals are concentrated in ore shoots, which may be enclosed in halos of low-grade material or separated by stretches of barren gangue minerals. The shoots have a wide range of size, shape, and continuity, ranging from small bunches or kidneys to great vertical or horizontal sheets, or to narrow vertical pipes. They may occur at places where there is a change in the strike or dip of the vein or in the character of the wallrocks, or at vein intersections. Recognition of such habits is useful in exploring for new ore shoots, although more subtle factors related to changes in the temperature, pressure, and chemistry may have been predominant in the precipitation of the ore metals. In the Coeur d'Alene district of Idaho, the highly productive Star-Morning ore shoot has a dip length of 6,700 feet, a strike length of about 4,000 feet, and a maximum width of about 50 feet (Hobbs and Fryklund, 1968, p. 1426). In contrast, the lead ore shoots in the North Pennine district of England, which are localized at the traces of relatively thin beds of hard limestone and sandstone along the vein, are as much as 3,000 feet in length but extend only 65 feet from top to base although they are locally connected with other overlying and underlying horizontal ribbon ore shoots by steep pipe-shaped ore shoots as much as 585 feet long (Dunham, 1949, p. 77–78).

In mineralogy and grade, the lead-producing ore shoots in veins are similar to the replacement and other type of ore bodies. The dominant minerals are galena and sphalerite and pyrite. In some deposits, argentiferous tetrahedrite, chalcopyrite, silver-lead sulfosalts, and, rarely, cobalt, nickel, and uranium minerals are also important. Gangue minerals commonly include quartz, siderite, calcite, barite, and fluorite. The grade of ore ranges from a few percent to as much as 50 percent or more combined lead and zinc. As indicated, many lead-producing veins are mined chiefly for their content of silver

and other metals, or for fluorite, barite, or calcite.

In addition to the great Coeur d'Alene district of Idaho and the North Pennine district of England, other examples of highly productive vein-type lead deposits include the classic districts of Clausthal, West Germany, Freiberg, East Germany, and Příbram, Czechoslovakia (Berg, 1927), Santa Barbara, Fresnillo, and Taxco in Mexico (Gonzáles Reyna, 1950), Morococha, Casapalca, San Cristobal, and others in Peru (Peterson, 1965), Butte, Mont. (Meyer and others, 1968), Montevecchio, Italy (Zuffardi, 1950), and many others. It should be noted, however, that some districts that are well known for other types of lead deposits, such as the Tintic, Park City, Leadville, and Pioche districts of the United States, and a great many others, also contain vein deposits of considerable importance.

The apparent environments of deposition of lead-bearing veins are generally as widely varying as the depositional environments of replacement deposits. They range in character from high-temperature veins containing galena in association with tourmaline (Knopf, 1913) and with garnet, hedenbergite, actinolite, fluorite, and quartz (Spurr and Garrey, 1908) to crustified epithermal veins that were deposited at low temperatures and shallow depths, commonly in association with fluorite, calcite, and quartz. The extreme temperature range may extend from 50°C to 550°C, and the pressure range from 1 to 1,000 atmospheres or more. Some veins, such as those of the Kentucky-Illinois fluorspar and lead district and possibly those of the North Pennine district of England (Dunham, 1949), are classified with the Mississippi Valley type deposits.

CONTACT PYROMETASOMATIC DEPOSITS

Although the irregular or pod-form lead deposits that occur in the aureoles of granitic plutons may have importance locally, particularly in Japan, they are relatively unimportant in terms of gross production. These deposits are localized chiefly in limy or dolomitic rocks that have become bleached, recrystallized, and silicated by solutions that were associated with intrusions of intermediate composition. Some deposits also occur in calcareous shales, tuffs, and sandstones. In general the contact deposits range in form from tabular bodies and masses of unpredictable shape to veins. The more common metallic minerals include galena, typically less abundant than iron-rich sphalerite, chalcopyrite, pyrite, pyrrhotite, arsenopyrite, and magnetite. In some deposits, bismuth, molybdenum, and tungsten minerals and native gold may also be present. The gangue minerals include diopside, hedenbergite, garnet, fluorite, epidote, actinolite, ilvaite, tremolite, quartz, and a variety of other silicates.

The deposits range in size from insignificant veins and lenses to large pods, one of which, at the Kamioka mine, Japan, is 850 feet long, 230 feet wide, and has been proven to a depth of 1,575 feet (Japan Geol. Survey, 1960, p. 182). This mine annually produces more than 1.5 million metric tons of ore containing 1.12 percent lead, 5.80 percent zinc, and 0.84 ounce per ton of silver. A somewhat similar but relatively lead-poor ore body in the Central district, New Mexico, 2,500 feet long, 30 feet wide, and 80 feet high (Lasky and Hoagland, 1950, p. 106), contained sphalerite and small amounts of galena and chalcopyrite, in association with andradite, salite, hedenbergite, ilvaite, and other minerals (Hernon and Jones, 1968, p. 1229). The average grade of this ore was probably close to 14 percent zinc, 0.13 percent lead, 6.19 percent iron, and 10.19 percent sulfur (Lasky and Hoagland, 1950, p. 106). Other contact pyrometasomatic deposits that produce lead include the Chichibu, Nakatatsu, Obori, and other deposits of Japan (Japan Geol. Survey, 1960, p. 180–183), Tetyukhe in Siberia (Grigor'yev, 1936), Parroquia-Magistral and La Sirena in Mexico (González Reyna, 1950), Falun, Garpenberg, Saxberget, Stollberg, Ammeberg, and other mines in Sweden (Magnussen, 1950), Trepča in Yugoslavia (Forgan, 1950), and possibly the Darwin mine in California (Hall and MacKevett, 1962). In some of these deposits lead is merely a coproduct or byproduct of zinc, copper, silver, or other metal.

The spatial and temporal relations of contact pyrometasomatic ore deposits with nearby intrusions indicate that hot, metal-enriched solutions rose steeply within the fractured margins of the plutons and spread laterally into the fractured and brecciated wallrocks. Where these wallrocks consisted of argillaceous and arenaceous limestone and dolomite, they were commonly converted to skarn and were also locally replaced by sulfide minerals and magnetite. The intimate association of galena, sphalerite, chalcopyrite, and other sulfide and oxide minerals with anhydrous garnet and pyroxene minerals and the thermodynamic stability of these metallic minerals above 600°C (Holland, 1965, p. 1140–1147) both indicate a depositional environment with temperatures and pressures not far below the solidification temperatures and pressure of the associated igneous rocks. These temperatures and pressures are above the critical constants for water, indicating deposition from supercritical solutions. It is recog-

nized, however, that the temperatures diminished with time and that some copper-zinc-lead deposits in contact zones are hydrothermal rather than pneumatolytic in origin.

RESOURCES

RESERVES

The reserves of lead contained in ores in known mines and districts in the world are here estimated to be about 141 million short tons, the equivalent of a 31-year supply at the 1971 rate of consumption, or a 22-year supply, not including recycled scrap, if an average annual increase in consumption of 3 percent is assumed.

These reserves are found on all of the continents except Antarctica, occurring in more than 40 countries, as shown in table 65. The greatest concentration of lead reserves is in the Southeast Missouri lead district; Weigel (1965, p. 77) estimates a potential of 30 million tons of contained lead for the Viburnum area alone. Other areas containing significant concentrations include south-central British Columbia and east-central New Brunswick in Canada, central Mexico, central Peru, the Balkan nations in Europe, the Kazakhstan and Trans-Baikal areas, U.S.S.R., and in particular, central, north-central, and other parts of Australia.

The estimate of reserves presented in table 65 compares with an estimate of 50 million tons of measured and indicated ore and a possibly equivalent amount of inferred ore made a decade ago by Callaway (1962, p. 2). The difference between the two figures possibly reflects in part a more conservative approach by the U.S. Bureau of Mines as compared with the Geological Survey, but it should be noted that Callaway's data preceded the discovery and development of enormous lead deposits in southeast Missouri, north-central Australia, Roumania, and elsewhere during the past 10 years. Recent unpublished Bureau of Mines estimates of the measured and indicated reserves of lead in the world are much closer to the estimates presented here.

The data presented in table 65 have been assembled chiefly from such sources as: Published estimates of tonnage and grade of ore reserves of specific mines and districts, which were based originally on physical exploration and geologically permissive extensions of known ore bodies, estimates made from narrative descriptions of the general size, character, and grade of less well developed deposits, and 10-, 20-, or 30-year projections of production data from long-term lead-producing countries for which specific reserve data or mine descriptions are not available. The validity and accuracy of these data are thus contingent upon a number of factors, including: The degree to which some ore bodies, particularly those of the irregular limestone replacement type, are accurately delineated more than a few years in advance of mining; the extent of current knowledge of the geology and ore habits within

TABLE 65.—*Estimate of world reserves [1] of lead, by regions or countries*

[In thousands of short tons]

North America:	
Canada:	
Yukon	3,500
Northwest Territories	1,250
British Columbia	5,000
Saskatchewan-Manitoba	200
Ontario	400
New Brunswick	4,500
Newfoundland	300
Other	700
Total, Canada	15,850
United States:	
Northeast Washington	150
Coeur d'Alene district	1,500
Butte district	500
Great Basin	2,500
Rocky Mountains	1,000
Tri-State	250
Southeast Missouri	30,000
Upper Mississippi Valley	1,000
Kentucky-Illinois	30
East Tennessee	10
Austinville district	100
Northern New York	45
Appalachian Massive:	
Sulfide Belt	100
Other	1,000
Total, United States	39,185
Greenland	70
Total, North America	54,105
Central America:	
Mexico	4,500
Honduras	250
Other	100
Total, Central America	4,850
South America:	
Argentina	1,000
Bolivia	800
Brazil	750
Chile	100
Colombia	25
Peru	3,500
Total, South America	6,175
Europe:	
Austria	175
Bulgaria	3,500
East Germany	500
Finland	100
France	700
Greece	300
Ireland	2,000
Italy	1,000
Norway	100
Poland	2,500
Rumania	500
Spain	2,750
Sweden	2,500
West Germany	4,500
Yugoslavia	3,000
Other	500
Total, Europe	24,525
Africa:	
Algeria	750
Morocco	1,500
South West Africa	1,500
Tanzania	100
Tunisia	400
Zambia	750
Other	200
Total, Africa	5,200
Asia:	
Burma	750
China	3,000
India	125
Iran	2,000
Japan	1,200
North Korea	1,800
Russia (U.S.S.R.)	18,000
South Korea	500
Thailand	20
Turkey	100
Total, Asia	27,495
Oceania:	
Australia	18,500
World total	140,950

[1] Reserves: Identified deposits from which minerals can be extracted profitably with existing technology and under present economic conditions.

specific districts; the common practice of maintaining secrecy about the development of new ore reserves or the loss of established reserves; and political and economic factors leading to a paucity of data from Communist nations such as China and the U.S.S.R. These factors may result in a margin of error of as much as 25 percent for some countries, but it should be noted that virtually all past estimates have erred in being considerably smaller than subsequent estimates based on more complete data and that most of the larger reserves are contained in deposits that are either well explored by drilling or extensively developed in operating mines.

In estimating lead reserves, price-cost and other economic factors should be considered together with technological advances in mining, milling, and smelting practices. The data of table 65 include all low-grade ores that can be mined at the currently prevailing relatively high price of lead. Decreasing prices and increasing costs will diminish ore reserves, and some of these ore reserves may be irretrievably lost if the higher grade parts of the deposits are mined, thereby eliminating the possibility of blending ores to produce acceptable mill feeds. Conversely, a price increase, or more expectably, technological advances that substantially reduce mining and milling costs or permit the utilization of complex ores, can abruptly increase apparent ore reserves by the inclusion of large tonnages of lead-bearing materials formerly considered to be unprofitable. In this category, in addition to conventional ores of subeconomic grade, are large volumes of lead-bearing slags, mill tailings, and mine wastes that are not considered in this report.

CONDITIONAL RESOURCES

Lead deposits of subeconomic grade have been recognized and explored to various degrees throughout the world, both on land and in the ocean basins. These deposits include not only conventional ore bodies that are similar to productive deposits except for a lower grade, but also unconventional deposits that previously have not been mined. The total quantity of lead in these presumed resources is not accurately known, but estimates of their contained metal—disregarding the potentially large problems inherent in achieving reasonable mining and metallurgical recoveries—may range as high as 1.5 billion tons of lead.

The predominant resource of low-grade lead-bearing material in this category is the manganese nodules that occur in considerable volume on parts of the ocean floor and on the beds of some freshwater lakes. Although these nodules are considered to be of potential value chiefly as a source of manganese, nickel, copper, and cobalt, they contain an average of about 0.10 percent of lead, which may be recovered in some of the hydrometallurgical processes now being investigated. Mero (1965) estimates 1.656 trillion tons of nodules for the Pacific Basin alone. These nodules contain an average of 0.09 percent of lead, approximately 1.3 billion tons. Over large areas where the nodules are particularly rich in nickel, copper, and cobalt, and where they presumably would be mined first, the average lead content is 0.18–0.30 percent and thus would be an important early coproduct. Similar deposits occur in the Atlantic and other oceans and in parts of Lake Michigan. Although mining and metallurgical reduction techniques are currently under investigation, no attempts at commercial exploitation have yet been made, and a question may be raised as to the validity of considering the nodules a mineral resource in the conventional sense at this time.

An example of another large but more conventional resource of subeconomic lead-bearing material is the famous Kupferschiefer and adjacent beds of the Zechstein and equivalent formations of Europe (Deans, 1950). Although this formation is best known and once was widely mined in East Germany for copper, it is believed to contain far greater quantities of lead and zinc, some of which was recovered as coproducts and byproducts. According to generalized estimates by Richter-Bernburg (1941), the portion of the Zechstein Formation extending between Magdeburg and Richelsdorf in East Germany alone may contain as much as 100–150 million tons of lead and 200–250 million tons of zinc as compared with only 50 million tons of copper. However, mining is not feasible under current economic conditions because of the limited thickness of the ore-bearing stratum, the relatively low tenor of the ore, the depth of large parts of the ore bed, and other factors. Mineral-bearing parts of the same stratigraphic unit also extend into West Germany, Poland, where it is currently being mined for copper, silver, and other metals, and northeastern England; the total quantity of their contained lead is not known but is probably much less than in East Germany.

Similar, but less well known, syngenetic deposits are currently being studied in the Belt Supergroup of northern Idaho and northwestern Montana. Preliminary estimates based on initial, incomplete surveys indicate a potential of 1 million tons or more of contained lead. However, the mining of adjacent and more valuable copper ore bodies may

result in a loss of the lead resources (A. L. Clark, oral commun., 1972).

Known and partly explored lead deposits of presumably large size also occur in strata-bound ore bodies in central Tennessee, central and south-central Missouri, northern Arkansas, central Texas, northeast Washington, and central Kentucky in the United States; in several areas in western Canada; in central Europe; in North Africa; and in the U.S.S.R. Other low-grade deposits are known in several mining districts in the Rocky Mountains and Great Basin, and in numerous districts that contain vein and replacement deposits in other parts of the world. Similarly, many low-grade, lead-bearing massive sulfide deposits in the Eastern United States have not been fully explored or developed, at least during recent decades, and some may contain significant recoverable resources. Eventual exploration and development of some of these low-grade deposits are expected to disclose, from time to time, sections that are of fairly high grade.

Another conditional, but perhaps unconventional resource of lead and other metals is the mineralized sediments that occur in the thermal deeps of the Red Sea basin (Degens and Ross, 1969). According to Bischoff and Manheim (1969, p. 535), the uppermost 10 meters of the Atlantis Deep in this basin contains 50 million metric tons of mineral-bearing sediment containing 3.4 percent of zinc, 1.3 percent of copper, 0.10 percent of lead, and about 1.6 ounces per ton of silver. The adjacent Discovery and Chain Deeps contain similar sediments of lower concentration, and presumably other undiscovered thermal areas in the world's ocean basins are the sites of metal-enriched sediments. Like the manganese nodules, exploitation of these deposits will pose many problems.

HYPOTHETICAL RESOURCES

Throughout the history of mining and exploration, only a few of the larger mining districts have been totally worked out and abandoned. Successive generations, armed with new concepts, new techniques, and new-found optimism, have successfully redeveloped old mines and discovered new deposits that were somehow overlooked by their predecessors. In many areas throughout the world, small or unimportant districts have also been developed into major producers. With the passage of time, mining has been carried to greater and greater depths, and new, totally concealed ore shoots and even centers of ore deposition have been discovered. Areas that hold promise for the discovery of new ore centers in active or formerly active mining districts include, among many examples, the central plateau of Mexico, the cordillera of Peru and adjacent countries, the districts of Kazakhstan that are undergoing accelerated development, and even the classic districts of Europe, United States, and Canada.

Like the "Identified Resources," the "Hypothetical Resources" include ores that are technologically recoverable as well as those that are subeconomic. Any attempt to quantify the amount of lead that may be contained in them would be perilous, but it may be generally estimated to be equal to half or more of the known world reserves.

SPECULATIVE RESOURCES

The volume of recoverable and subeconomic lead ores in undiscovered districts cannot be estimated, but they may equal or exceed all of the reserves currently known throughout the world. During the past few decades, new mines and ore centers that rank among the largest that are known have been discovered in Canada, Australia, United States, and other countries throughout the world. These deposits occur in a variety of geologic terranes, but had remained undiscovered because they were totally concealed by barren rocks or because insignificant exposures did not indicate their true size or grade. Inasmuch as vast areas of possible mineral-bearing rocks underlie glacial debris in North America, Europe, and Asia, deep soil and other surficial deposits in the tropic, temperate, and arid regions of the world, and even the marine waters of the continental shelves, it is certain that similar deposits will continue to be discovered during the indefinite future. Many of these deposits are amenable to discovery through geophysical and geochemical exploration; others, such as those that are thoroughly oxidized or deeply buried, will be discovered only as a result of imaginative geologic analysis and courageous physical exploration. Inasmuch as lead deposits are widely distributed in many different geologic environments throughout the world, such geologic analysis will be applied most successfully to specific types of lead deposits in specific geologic terranes. As in the past, it will be chiefly based on continuing studies of the genesis of ore deposits and the features that determine their distribution and localization in the earth's crust, and it must be coupled with a willingness to consider and test pioneering concepts of ore deposition and distribution.

PROSPECTING TECHNIQUES

The principal new discoveries of lead deposits like most other types of mineral deposits, have been

made mainly in existing mining districts through direct physical exploration of undeveloped areas that are geologically similar to the environments of the known ore deposits. In previously unproductive but geologically favorable terranes and in small or relatively inactive districts, the preliminary techniques of exploration employed in advance of drilling, shaft sinking, or drifting are less direct and may be divided into three categories: geologic, geochemical, and geophysical. These techniques may be used separately or in any combination or sequence. Prior to World War II and the era of accelerated exploration that followed it, some new discoveries were chance finds or were made through serendipitous observations during unrelated efforts. As noted by McKinstry (1948, p. 413), however, such lucky accidents often make entertaining anecdotes but are not the source of many mine discoveries. Most modern discoveries result from scientifically directed prospecting, a costly undertaking.

Geologic techniques for prospecting for lead deposits range in magnitude from the regional delineation of mineral belts, greenstone belts, and other metavolcanic terranes and areas of domal uplift on cratonic platforms to the solution of the problem of fault displacement of part of a minor ore body—all based on geologic mapping at appropriate scales. Features to be recognized and evaluated, especially in the search for concealed deposits or deposits with unimpressive surface manifestations, are structural and stratigraphic localization of ore, chemical and mineralogical changes in the adjacent wallrocks, zonation, and temperature and pressure regimes. Among many examples of mineral discoveries based largely on geologic reasoning are the lead deposits of the Viburnum area, Missouri, the lead and zinc deposits of central Tennessee, and on a smaller scale, the polymetallic Bulldog Mountain mine, Creede district, Colorado (Steven and Ratté, 1960; Cox, 1965).

Geochemical exploration is generally used in conjunction with geologic studies in several ways: to help eliminate unmineralized tracts within broad areas that are geologically favorable, to identify halos of dispersed metals in rocks or in residual surficial deposits above and adjacent to concealed deposits, to delineate the source areas of ore-metal dispersion trains in transported materials such as stream sediments and glacial till, and to determine possible patterns of compositional zonation of known deposits or groups of deposits. The techniques used include chemical, spectrographic, radiometric, and atomic-absorption analysis, heavy-mineral dispersion studies, and analysis of geobotanical relations (Hawkes, 1957). Examples of lead-producing mines that were discovered, at least in part, by geochemical techniques, include among others the Laisvall, Rakkejaur, and other deposits in Sweden (Grip, 1953), the Burgin deposit, Utah (Bush and others, 1960), and the Tynagh ore body in Ireland (Clark, 1965).

Geophysical prospecting techniques are based on certain physical characteristics of ore minerals, ore bodies, or ore host rocks that contrast with their enclosing country rocks and may be detected, measured, and evaluated rapidly, cheaply, and usually at some distance from the body being sought or through a concealing cover. Such characteristics include density, magnetism, electrical conductivity, radioactivity, and seismic response. In the search for metallic mineral deposits, including galena ore bodies and especially polymetallic sulfide deposits containing galena in association with high proportions of pyrite and pyrrhotite, the most successful methods during the past decade or so have been airborne magnetic and electromagnetic surveys that establish the position, size, and trend of anomalies over large areas of till-, forest-, or swamp-covered terrane, followed by detailed ground surveys that employ other geophysical, geochemical, and geologic techniques. These methods have been especially successful in the Precambrian shield areas of the world where large massive sulfide deposits are concealed beneath a relatively thin cover of surficial material. The aeromagnetic surveys delineate greenstone belts, intrusive bodies, major faults, and other geologic features that are commonly concealed. The electromagnetic (EM) systems are then used to create a low-frequency inductive field in the vicinity of the low-flying aircraft, inducing eddy currents in the conductive ore bodies; the secondary fields radiating from the conductive bodies are then detected by receivers. The application of EM techniques has been greatly enhanced in recent years by the development of rapid data-processing equipment coupled directly to the transmitting and receiving equipment. Other techniques that may be used concurrently with airborne magnetic and electromagnetic methods include infrared and radar imagery, color and multiband photography, and side-viewing radar.

Geophysical techniques used on the ground in the evaluation of anomalies discovered by airborne methods include a variety of EM systems that are similar to the airborne EM systems, the long-established and widely used induced polarization (IP) methods, and the audiofrequency magnetic (AFMAG) method, which utilizes natural currents of the earth that arise chiefly from thunderstorm activity in the equatorial regions. Locally, resistivity and self-potential methods also continue to be used. Each of these systems

may be somewhat limited, or have special applications, when used in the search for specific types of ore bodies. In general, the surface EM systems have been most successfully applied in the exploration for massive sulfides beneath thin glacial overburden; the IP systems are widely used in the exploration for disseminated sulfides of the porphyry copper or Mississippi Valley types, although disseminated barren pyrite, graphite, and some clay minerals also give IP responses. The AFMAG system is useful in locating deep conductive features and can be used to trace major faults and belts of rocks that have a wide range of conductivity.

Many important lead-producing deposits have been discovered as a result of geophysical prospecting. These include the Brunswick, Heath Steele, Kidd Creek, and many others in eastern Canada, the Lady Evelyn in northern Australia, the Gortdrum and Silvermines deposits in Ireland, deposits in the Skellefte area, Sweden, the Vihanti district in Finland and others (for a more complete list see Pemberton, 1966, and other sources).

PROBLEMS FOR RESEARCH

The reserves and identified world resources of lead, unlike resources of many other mineral commodities, appear to be adequate for the foreseeable future. Despite an accelerating rate of consumption since World War II, these reserves and resources have not only kept pace with extraction but have been substantially increased as a result of highly successful exploration in many countries. Enormous submarginal resources have been recognized in the ocean basins in the form of heavy-metal-rich manganese nodules, which eventually may become a competitive source of lead. It would appear that the main problems concerning lead are related not so much to the availability of resources as to mining, processing, and use of lead in our modern mechanized society. As these aspects are beyond the scope of this paper, they are noted here only briefly.

Of chief concern is the toxicity of lead to humans, resulting in a variety of health hazards, particularly in the urban environment, and the resultant loss of markets for some lead products as selected uses of lead are restricted or prohibited. For example, recent legislation has virtually eliminated the use of lead pigments in interior paints and greatly restricted their use in many exterior and industrial applications. Similarly, legislative action has been directed toward reducing or eliminating lead in high-octane gasoline. Although such action may be required to bring about the adoption and use of some catalytic exhaust-control devices and to prevent atmospheric contamination, the advantages of tetraethyl lead in controlling the burning rate of gasoline in high-compression engines, which greatly decreases the consumption of gasoline under conditions of constant performance, may force the adoption of smog-reducing exhaust systems that are compatible with at least a small quantity of lead in most gasolines, or that remove lead along with carbon monoxide, nitrogen oxides, and unburned hydrocarbons. Other factors leading to decreased use of lead include the expanding use of plastic cable sheaths and caulking compounds and the use of alternate compounds in solder, type metal, and coatings.

Despite these restrictions on the use of lead, increased consumption is anticipated as a result of the accelerating use of automobiles and trucks throughout the world, the development of battery-operated vehicles for delivery and commuter transport, the growing demand for lead as an additive to improve the machinability of steel, brass, and other alloys, and the small but possibly increasing use as radiation shielding that will be required in the wider adoption of atomic energy.

More directly related to the problems of reserves and resources are the many difficulties inherent in utilization of fine-grained, complexly intergrown massive ores that constitute an important part of the reserves of lead and other metals in southeastern Canada, Eastern United States, Japan, and elsewhere. Despite many attempts, some of these ores have not been amenable to processing efficiently or profitably by conventional milling and smelting techniques. Continued development of chemical ore-processing methods and of continuous-smelting techniques that do not require clean separation of galena, sphalerite, pyrite, and copper sulfide minerals should lead to greater development of these massive sulfide ore bodies.

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LIGHTWEIGHT AGGREGATES

By A. L. Bush

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ABSTRACT OF CONCLUSIONS

The United States is adequately supplied with both structural lightweight aggregates (scoria, volcanic cinder, pumice and pumicite, expandable clays, shales and slates, diatomite, expanded blast-furnace slag, and fly and bottom ash) and ultralightweight aggregates (expanded perlite, expanded pumicite, and exfoliated vermiculite). The aggregates are low unit value, high place value materials, partly because large quantities are available and partly because normal-weight (sand and gravel) and synthetic aggregates are stiff competition. However, they have high place value, in as much as transportation costs largely determine whether they are used.

Recoverable reserves of expanded clays, shales, and slates are equivalent to about half the cumulative output needed through the year 2000. For the same period, scoria, cinder, pumice, and pumicite reserves are at least twice the estimated demand, and perlite reserves seem to be at least as large, and vermiculite reserves somewhat larger than their respective demands.

Virtually no export or import markets exist for the lightweight aggregates. Along the eastern seaboard, oceanic freight rates allow competition between pumice from western domestic sources and pumice imported mostly from the Mediterranean area, but only a few hundred thousand tons per year are involved. For similar reasons, a few thousand tons of vermiculite are imported annually from the Republic of South Africa. A few thousand tons of domestic perlite are exported to Canada per year.

The prospects for converting hypothetical and speculative resources of clays, shales, scoria, cinder, pumice, and pumicite to recoverable reserves are excellent. For perlite and vermiculite, the prospects are good.

FOREWORD

Many materials serve primarily as lightweight aggregates for concretes and plasters, but some of them find even more use as construction materials in their own right, as components in manufacturing processes or in end products, or as aids of various kinds in agriculture. Some are used for their physical properties alone, but for most the chemical properties also are significant. Some are used with only minimal processing, such as crushing and grading, but others require fairly complex and sophisticated

treatment. Many are mineral raw materials, others are waste or synthetic products, and some are organic materials. A brief look at the array of materials and at some of their properties is given in table 66. Several of the materials touched on in this chapter are also discussed in other chapters. (See "Abrasives," "Clays," "Diatomite," "Pigments and Fillers," "Magnesian Refractories," and "Silica Sand.")

The distinction between normal-weight and lightweight aggregates is made at about 75 lb per cu ft (pounds per cubic foot) for loose graded aggregate. Most lightweight aggregates weigh considerably less; generally those used for structural purposes are in the 35- to 60-pound range and those used for non-load-bearing purposes are in the 5- to 20-pound range (ultralightweight aggregates).

Expanded clays and shales make up more than 70 percent by weight of the structural lightweight aggregates used annually, with the remainder divided among expanded slate, scoria, expanded slag, and fly ash at about 6, 7, 15, and 2 percent, respectively. The production data for clays and shales are commingled and cannot be separated satisfactorily, but about half of all the aggregate seems to be made from expanded shale.

Vermiculite and perlite are the most used ultralightweight materials, each with about one-third

TABLE 66.—*Classification and properties of lightweight aggregate materials*

Materials	Composition (weight percent)	Texture (unexpanded)	Expansion needed	Texture (expanded)	Weight (lb per cu ft)	Remarks
Products of explosive volcanism						
Pumice	Silicic	Frothy, very vesicular.	None	Unchanged	30–60	Blocks and fragments of coherent glass.
Pumicite	---do	Porous	---do	---do	60–70	Shards of glass; very fine grained; very low strength; expansible.
Scoria	Basic	Clinkerlike, very vesicular.	---do	---do	35–75	Tephra as bombs and lapilli; vesiculated zones in lava flows.
Perlite	Silicic (H_2O:2–5)	Fractured, onionskin partings.	To × 5; about 1,400°F.	Cellular, frothy spheres.	6–16	Low strength; high permeability to surface area ratio; ultralight.
Obsidian	Silicic (H_2O:<2)	Dense glass, conchoidal fracture.	To about × 5; 1,400°–1,500°F.	---do	25–30	Do.
Deposits of sedimentary origin						
Clays, shales, slates.	Wide range; silty, calcareous, carbonaceous, ferruginous.	Dense, may be fissile.	To × 2–3 at about 1,800°–2,200°F.	Cellular, fairly uniform.	30–60	Kiln or sinter product; good strength; red ores least likely to expand.
Diatomite	SiO_2, close to 100, may be clayey, petroliferous.	Porous, may be friable.	None	Cellular	30–50	Coproduct of calcining for filter aid products.
Alteration of mafic silicate minerals						
Vermiculite (Hydrobiotite).	Hydrated magnesium-iron-aluminum silicates; varies considerably.	Micaceous	To × 8–15 at about 2,000°F.	Accordionlike	6–15	Supergene alteration of biotite, phlogopite, hornblende, diopside, augite, olivine, chlorite, serpentine; low strength; ultralight.
Byproducts of manufacturing processes						
Blast-furnace slag.	Best slag is SiO_2=35–38; CaO+Al_2O_3=44–47; low MgO, FeO, S.	Liquid slag	About ×3 at ambient temperature.	Cellular, fairly uniform.	35–60	Zinc and phosphate smelter slags have also been used successfully.
Fly ash, bottom ash, coke breeze.	Wide ranges; SiO_2+Al_2O_3+Fe_2O_3:>70, MgO:<5; SO_3:<3; alkalies:<1.5.	Extremely fine grained.	None	Cellular	35–55	Ash from burning pulverized coal; sintered to cause agglomeration.
Cinders	---do	Cellular, nonuniform.	None	Unchanged	40–60	From burning of pea-size or larger coal, coke.
Synthetic and miscellaneous materials						
Plastic beads and foams.	Polyurethane, polystyrene, polyvinyl chloride.	Does not apply	Various temperatures, reactions.	Cellular, uniform spheres.	<15	Many patented techniques and applications.
Foaming compounds.	Aluminum powder, vinyl resins, H_2O_2.	---do	---do	Does not apply	Various	Does not substitute for aggregate; lowers density by adding voids.
Rice hulls, wheat hulls, sawdust, wood fibers.	Organic	Fibrous, cellular.	None	Unchanged	No data	Generally low strength; very minor usage.

share of the market for aggregates. Pumice-pumicite and diatomite claim the remaining third in about a 10:1 ratio. The production data for pumice, pumicite, scoria, and volcanic cinders are so commingled and the terms are applied so unspecifically in regard to uses that only the broadest guess can be made; the ratio for pumice-pumicite may be low by a factor of 3.

All in all, about 13.5 million short tons of rock was used in 1970 for structural lightweight aggregates, and perhaps as much as one-half million short tons was used for ultralightweight aggregates for non-load-bearing concretes, plaster insulation board, and loose fill insulation. Their values after processing for final use were about $71 million and $14 million, respectively. As these materials also have other applications, their annual production value for all uses was somewhat greater for the structural lightweights, about $74 million, and much greater for the ultralightweights, about $78 million; we have an overall value, then, of more than $150 million per year.

The natural subdivision of the lightweight aggregates into those used for structural purposes and those used in non-load-bearing applications will be followed in this chapter.

STRUCTURAL LIGHTWEIGHT AGGREGATES

INTRODUCTION

Despite their varied origin, the aggregates suitable for structural purposes have several characteristics in common: they are porous, ideally highly so; they are permeable, ideally poorly so; and the pore walls are relatively thick, as compared with the diameter of the voids. This last characteristic gives the aggregates fairly high compressive strengths. The porosity of all aggregates results from heat treatment—natural (volcanic) heat for the scoria; intentional rotary kilning or horizontal furnace sintering for the expanded clays, shales, and slates; and unavoidable heat in blast furnaces for the slags and in coal-fired steam power plants for the fly ash.

Because of their porus but fairly impermeable texture, the lightweight aggregates are both thermal and acoustic insulators. These properties make the aggregates desirable for bulk use in floor and roof fill, and they are an added advantage in concretes where the primary reason for the use of these aggregates is weight reduction.

Compressive strength that can be obtained for concrete made with these aggregates ranges from perhaps 1,200 psi (pounds per square inch) to more than 6,000 psi, depending upon the proportions of sand, cement, aggregate, and water. Higher strength and increased weight go hand in hand; for example, a scoria aggregate concrete at 1,200 psi weighs about 60 lb per cu ft, whereas a sintered expanded shale concrete at about 6,000 psi weighs about 120 lb per cu ft. In this broad range of strengths, the lightweight aggregate concretes can be used for fill, bridge decks, shell walls, concrete floors, concrete frames using precast, prestressed, or posttensioned girders, precast tilt-up units, poured barge and ship hulls, and lightweight masonry blocks. In bulk form the aggregates are used as railroad ballast, as highway and embankment fill, and in the surface course of bituminous paving mixtures.

Structural lightweight aggregates and concretes play an important though not indispensable role in urbanized, industrialized nations. They enhance efficiency—they allow buildings to be made higher, their steel framework to be more fire resistant, and their floors and ceilings to be better insulants. They contribute to more economical use of funds, materials, and time, inasmuch as concrete can be pumped higher and farther from a single location; plates, girders, and shell walls can be mass produced offsite; and additional thermal and acoustic insulation can be reduced. On the esthetic level, the lightweight aggregates and concretes allow innovative, experimental construction and design.

The United States is by far the largest producer and consumer of structural lightweight aggregates. Inasmuch as domestic supplies are abundant and the materials have low unit value but high place value—that is, transportation costs largely govern whether the materials can be used—there are virtually no import or export markets. To all intents, the country is self-sufficient in these commodities. Production data for pumice reveal some imports used for lightweight block, but in 1970 less than 400,000 tons was imported for all purposes, as compared with more than 8 million tons of domestic lightweight aggregates used in lightweight block. Overall, imports make up less than 2 percent of the structural lightweight aggregates market. Almost all this usage was along the eastern seaboard, where marine freight rates allowed competition with pumice from domestic western sources.

EXPLOITATION

Pumice first was used as a lightweight construction material by the Romans about the beginning of the Christian era, but because production data are somewhat sketchy between then and about 1940, only the production trends since 1940 are really of

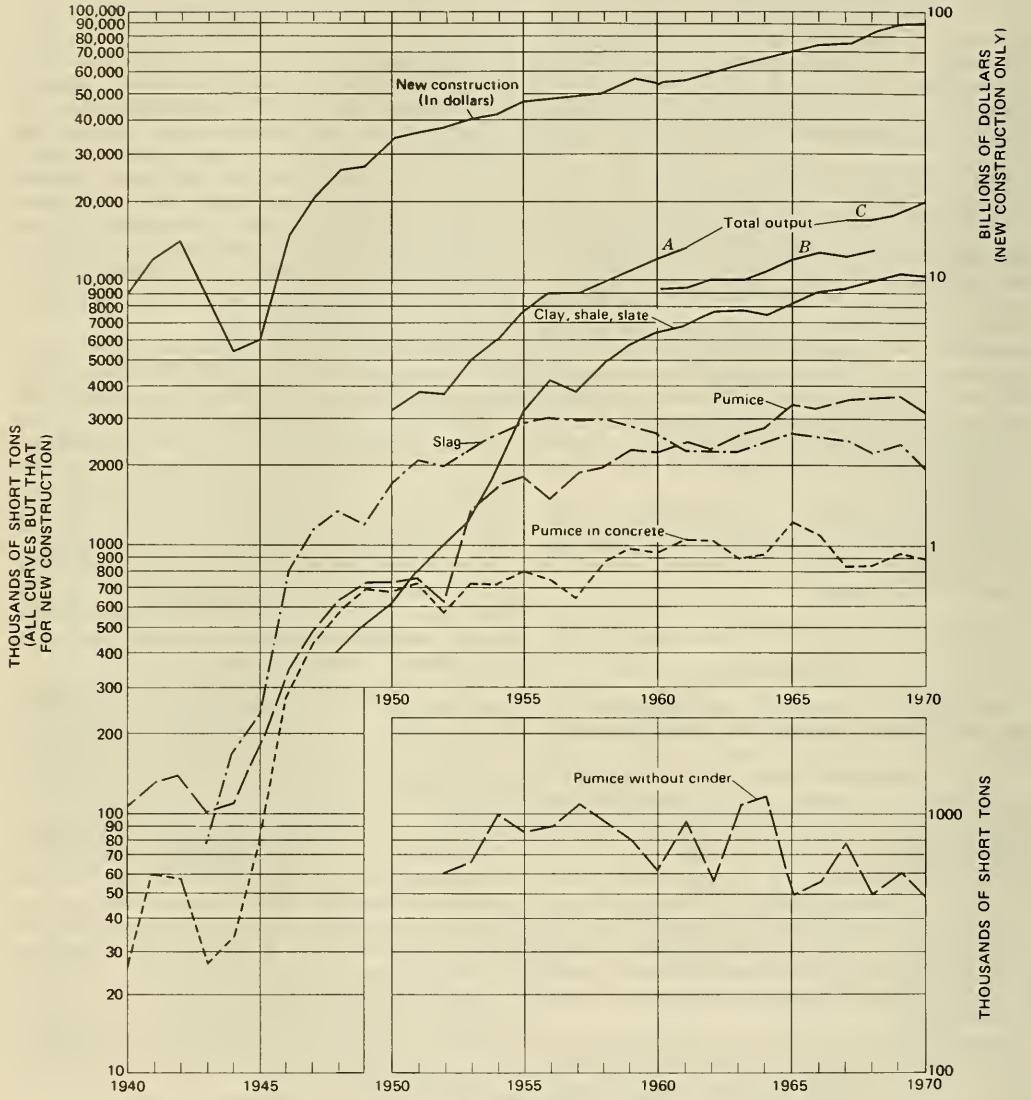

FIGURE 40.—Production of materials used as structural lightweight aggregates in the United States, 1940–70.

New construction.—Value of total new construction, exclusive of maintenance and repair; data from Statistical Abstracts of the United States, 1940–70.

Total output.—Tonnage of all materials used as structural lightweight aggregates: *A*, Estimate in Rock Products, v. 65, no. 1, p. 83, 1962. *B*, Estimate by R. A. Grancher in Rock Products, v. 72, no. 12, p. 62, 1969 (lacks data for slate, 1960–63). *C*, Estimate by Harvey Smith in Mining Engineering, v. 24, no. 1, p. 53, 1972.

significance. Cinders from coal-fired furnaces and boilers were used throughout the country for the production of cinder block from the late 1800's through World War II; conversion to gas- and oil-fired installations and to the use of pulverized coal has effectively removed the source of the material, and it now constitutes a very small resource. Fly ash and bottom ash, the residues of pulverized-coal combustion, are used as aggregates and pozzolans and will supply an increasing amount over the next several years to the aggregate market. Expanded clay and shale aggregates in lightweight concrete were used as early as World War I in concrete ships, and there was a small market (small, partly owing to patent restrictions) for the lightweight aggregates through the end of World War II. A rapid increase in number of plants and production of expanded clay and shales began in about 1947 (fig. 40) with the expiration of patents on the rotary kiln (Hayde) process. Data before 1953 are incomplete but suggest that production tripled from 1947 to 1953 and tripled again between 1953 and 1956. Production and consumption of "pumice" and expanded iron blast-furnace slag increased very rapidly in the period 1945–50 (fig. 40), as a part of the postwar construction boom. Since 1956 overall production of the structural lightweight aggregates has reflected construction trends fairly closely, although some deviations from trend in production of pumice and a long-term decline in production of expanded slag have occurred.

A fairly steady increase (with some minor fluctuations) in the total amount of pumice produced since 1957 conceals sharp periodic (1–2 years) variations in the amounts classed as "volcanic cinder" (fig. 40); inconsistency in classification probably causes the variation, rather than actual selective production. Deviations in trend between total pumice and pumice used as concrete aggregate and admixture are real, however, and reflect the responsiveness of the lightweight concrete-block market to construction activity in the residential and light industrial fields. Since 1953 the production of all pumice has more than doubled, whereas its use in concrete has increased more slowly and has virtually leveled off since 1958–59, fluctuating about 10 percent around the million-ton-per-year level. During the same period use of pumice as railroad ballast decreased, but its use for road construction very markedly increased.

Expanded slag production peaked between 1955 and 1958, and it has slowly declined since then, hovering at about 2–2½ million tons per year. Significant short-term decreases reflect both market conditions, as in 1961, 1968, and 1970, and nonmarket influences, as in the prolonged steel strike of 1959, which cut off supplies of molten slag. Overall, the decline represents a loss of markets to competitive products, particularly the expanded and sintered clays, shales, and slates. Sources of slag predominantly are iron blast furnaces, which are in only a few areas of the country. Suitable sources of clay, shale, and slate are widespread; new facilities have been brought into production to compete with slag in market areas close to the furnaces, as well as in the peripheral areas where slag use a marginal operation. Usage of fly ash in some of the slag-production areas has also contributed to the decline.

In common with other extractive industries that produce materials at the earth's surface, the lightweight-aggregate industry is faced with the environmental problems inherent in open-cast mining, in the control of fine materials formed in the manufacturing process, in the destructive consumption of water in some processes, and in the degradation of water quality in other processes. None of these problems is insuperable; all involve extra expense in production, in a highly competitive market with commonly slender profit margins. As low-unit-value high-place-value commodities, raw-material sources and production sites have to be as close together as possible, and both have to be as centrally located to the market area as possible. Consumption of structural aggregates is mostly in urban areas; environmental impacts and conflicts are increased because they take place close to where many people live. One further complication; in some areas the

Clay, shale, slate.—Total production of kilned and sintered aggregate: 1948–55, J. W. Roberts, Solite Corp., oral commun., Feb. 14, 1960; 1956–70, U.S. Bur. Mines Minerals Yearbooks, and A. L. Bush, U.S. Geol. Survey.

Slag.—Expanded blast-furnace slag, does not include zinc and phosphate smelter slags; U.S. Bur. Mines Minerals Yearbooks.

Pumice.—Total tonnage of pumice and pumicite, 1940–70, and of scoria and volcanic cinder, 1953–70; U.S. Bur. Mines Minerals Yearbooks.

Pumice in concrete.—Tonnage used as concrete admixture and additive, excludes scoria and volcanic cinder before 1953; U.S. Bur. Mines Minerals Yearbooks.

Pumice without cinder.—Tonnage of pumice and pumicite, exclusive of scoria and volcanic cinder, 1953–70; U.S. Bur. Mines Minerals Yearbooks.

raw material must be extracted before the area is irretrievably lost to preclusive uses, such as industrial plants, high-rise buildings, and residential construction.

CLAYS, SHALES, AND SLATES

Many varieties of clays, shales, and slates, of diverse origins, expand somewhat on heating to about 2,000°F (1,100°C). Basically, all clays, shales, and slates are chemically and, to some extent, mineralogically similar—they differ mostly in their physical characteristics. Lightweight aggregates are used only for their physical properties, and it is their chemical similarity that makes all of them amenable to thermal expansion. Table 67 presents several representative chemical analyses for the argillaceous rocks that have been tested for use as lightweight aggregate. The range in composition is wide for each of the three materials, and all three ranges largely overlap. Unfortunately, the analyses of rocks that expand suitaby, that expand inadequately, or that do not expand, all fall in these same ranges.

The basic requirement for expansion of an argillaceous rock is a source of gas within the raw material, but several other physical characteristics are required for full suitability. Sufficient gas must form to cause a full bloat, in the temperature range where the material is pyroplastic (melted enough to be viscous), so that the gas can be trapped; there must be enough vitrification, at a high enough viscosity, so that most of the gas can be held in small, evenly distributed pores; and the temperature range between softening and liquefaction must be large enough (about 100°F) that the bloating can be controlled in large-scale commercial production. Economical production is had at kiln or sinter temperatures between 1,800° and 2,200°F (1,000°–1,200°C), although temperatures can be as low as 1,600°F (870°C) or as high as 2,400°F (1,300°C).

There is little agreement on the relative importance of the number of possible sources for the gas evolved within the raw material. Conventional wisdom in the early days of the industry held that the argillaceous rocks had to have a significant organic content, although the amount varied with the practitioner. However, laboratory investigation of the evolved gases showed that many materials with very little total carbon expanded better than those with an appreciable amount (Austin and others, 1942; Sullivan and others, 1942)—to perhaps 1.5 percent—and that CO_2, SO_2, and H_2O all played a part in the bloating. Riley's (1951) research indicated that thermal destruction of hematite, pyrite, and dolomite provided both CO_2 and SO_2 in amount sufficient for bloating without recourse to organic carbon. Ehlers and Richardson (1958) emphasized the role of CO_2 derived by the heating of calcite, dolomite, and ankerite in the argillaceous rocks, and subsequent more effective entrapment in illite than in kaolinite (kaolinite fuses at a higher temperature than illite). They deemphasized the role of iron in gas liberation, considering it to be of possible significance only where hematite exceeded 5 percent of

TABLE 67.—*Comparative composition of expansible clays, shales, and slates*

Sample	Clay			Shale			Slate		
	1	2	8	4	5	6	7	8	9
SiO_2	63.00	61.80	36.7	49.00	65.01	69.00	64.6	54.00	57.36
Al_2O_3	20.74	16.88	25 8	24.67	17.07	11.60	12.9	17.30	18.96
Fe_2O_3	4.27	[1]9.68	2.65	5.44	2.16	6.37	1.72	[1]6.65	[1]7.12
FeO	2.30		.13	5.79	3.38	1.07	4.17		
MgO	1.82	.06	1.22	2.36	1.89	1.58	1 36	3.32	3.69
CaO	.66	1.27	10.7	.49	.70	.32	1.29	4.68	3.02
Na_2O	.51	2.09	.26	.74	1.33	.95	1.28	.76	.61
K_2O	3.4	.67	3.4	3.60	2.59	3.00	5.9	2 28	2.24
TiO_2	1.06	1.17	.57	----	----	.80	1.10	.73	.78
Loss on ignition	----	7.36	----	8.16	6.69	6 24		4.87	6.98
Total	[2]99.74	100.98	[2]102.01	100.16	99.81	[2]101.20	[2]100.00	[2]100.13	99.75
CO_2	.32	----	2.93	.98	.21	.37	3.47	4.21	2.96
C (organic)	.73	----	.72	.87	.80	.36	.64	1.34	----
H_2O+	7.15	----	4.68				1.18		
H_2O-	2.81	----	4.28	.79	.64	.51	.41	----	----
S	.04	----	.08	----	----	.044	.08	----	----
Other	[3].93	----	[4]7.89	----	----				

[1] Total iron.
[2] Total of all constituents.
[3] P_2O_5, 0.57; MnO, 0.11; Cl, 0.16; F, 0.10.
[4] P_2O_5, 7.3; F, 0.59.

SAMPLE LOCATIONS AND REFERENCES

1. Pennsylvania (Roen and Hosterman, 1969, sample Ro–R–1b).
2. New South Wales, Australia (Hill and Crook, 1960, sample 4).
3. Florida (Conley and others, 1948, sample 10).
4. Illinois (White, 1960, sample 1416).
5. Illinois (White, 1960, sample 1334A).
6. Pennsylvania (Root, 1968, sample 10).
7. Florida (Conley and others, 1948, sample 3).
8. Pennsylvania (Conley, 1942, sample 1).
9. New South Wales, Australia (Hill and Crook, 1960, sample 18).

the rock. Meanwhile, Gervids (1957) admitted that carbonates, sulfides, sulfates, and oxides could all participate in the gas-forming process but asserted that the gas was formed at temperatures (550°–825°C) well below the rock-softening level (1,050°–1,150°C). He suggested that only the dehydroxylation of micas and amphiboles could account for the bloating, inasmuch as these reactions occurred at rock-softening temperatures. Hill and Crook (1960, p. 382) specifically refuted this contention, stating that it was intrinsically "improbable because the dehydroxylation temperature is considerably lower than the bloating temperature * * *," and they very strongly emphasized the role of the reduction of ferric to ferrous oxide, with the oxygen evolved as the cause of the bloating. Chopra, Lal, and Ramachandran (1964) decided that both organic matter and calcium carbonate produced the gas that does the bloating, and that hydroxyl water, entrapped pore air, and ferric oxide were not significant contributors. Donnelly, Brennan, and Peacock (1968) concluded that iron oxide and water reacted with carbon (as little as 0.1 percent) to produce carbon monoxide, carbon dioxide, and a little hydrogen and that the decomposition of carbonates does not contribute to the bloating. This brief history suggests (1) that the divergence of opinion as to what causes bloating is considerable, (2) that no single factor is most important, and (3) that insufficient consideration has been given to the possible effects of the suggested reactions operating simultaneously, at least as far as the production of gas is concerned.

Riley (1951) investigated the combinations of constituents that apparently acted as fluxes and affected pyroplastic conditions at the appropriate temperatures for gas formation and retention. In plotting the distribution of some 85 chemical analyses of bloating and nonbloating clays and shales in terms of their SiO_2, Al_2O_3, and combined Fe_2O_3, FeO, CaO, MgO, and $(K, Na)_2O$ (flux) content, he was able to define a range of compositions that included most of the bloatable materials and excluded most of the nonbloatable materials. That range was about SiO_2, 52–80 percent; Al_2O_3, 11–25 percent; and combined fluxes, 10–25 percent (fig. 41). Additional investigations since 1951 have shown that this bloating range is less reliable than it first seemed to be, but it is a useful guideline. As examples, White (1960) showed that the range had to be extended in the direction of higher Al_2O_3 and lower flux contents, whereas Sweeney and Hamlin (1965a) had to extend the range to a higher flux content (fig. 41). At the same time, more materials previously considered to be nonbloatable were included in the bloating range.

Laboratory methods for evaluating raw materials have been described by Conley, Wilson, Klinefelter, and others (1948), Klinefelter and Hamlin (1957), and Hamlin and Templin (1962). The ultimate evaluation is how the material expands in a commercial operation; for this determination to be made, several tons of material may need to be run.

To distinguish between favorable and unfavorable rocks in the field is difficult because so many different argillaceous rocks have been found to be suitable. Burnett (1964) suggested that field estimates be made of the content of iron, alkali, carbonate, organic carbon, and silt. Because too much of any of these constituents can cause the bloating range to be too narrow, the firing temperature to be too high, or the expanded product to be too heavy, an overabundance can serve as a negative criterion. There are no really positive field criteria. Illitic and montmorillonitic sediments seem to be more consistently favorable than kaolinitic ones. The darker colored clays, shales, and slates (green, gray, black) are more suitable than the light colored (particularly red) ones, especially if they have a moderate content of dispersed organic carbon. In general, unweathered materials are more suitable than weathered ones. Common or brick clay is more suitable both physically and economically than flint or ball clay. Thinly fissile shales and slates tend to expand unidimensionally, which is undesirable. Most of these features tend to vary more greatly in short vertical intervals across the sedimentary section than laterally along the sedimentary units, but lateral variation is enough that units unsuitable at one point may be eminently suitable a few hundreds of yards to a few miles away.

In addition to the materials that can be made to expand, argillaceous rocks can be ground, mixed wth combustible materials—such as ground coal—and sintered to produce lightweight aggregates. The mass becomes pyroplastic, or cohesive, and voids are left as the combustibles are burned out; some bloating may occur, but it is incidental to the sintering. Inasmuch as units that may not bloat of themselves can thus be used for lightweight aggregate, classifications of argillaceous rocks as unfit is unwise unless the rocks have been tested and found unsuitable for both processes.

Marine, littoral, lacustrine, and fluviatile clays and shales, and slates derived from them, are all possible raw materials. They occur in formations that range in thickness from a few feet to more than 1 thousand feet and in age from Precambrian to Holocene, and they are distributed throughout

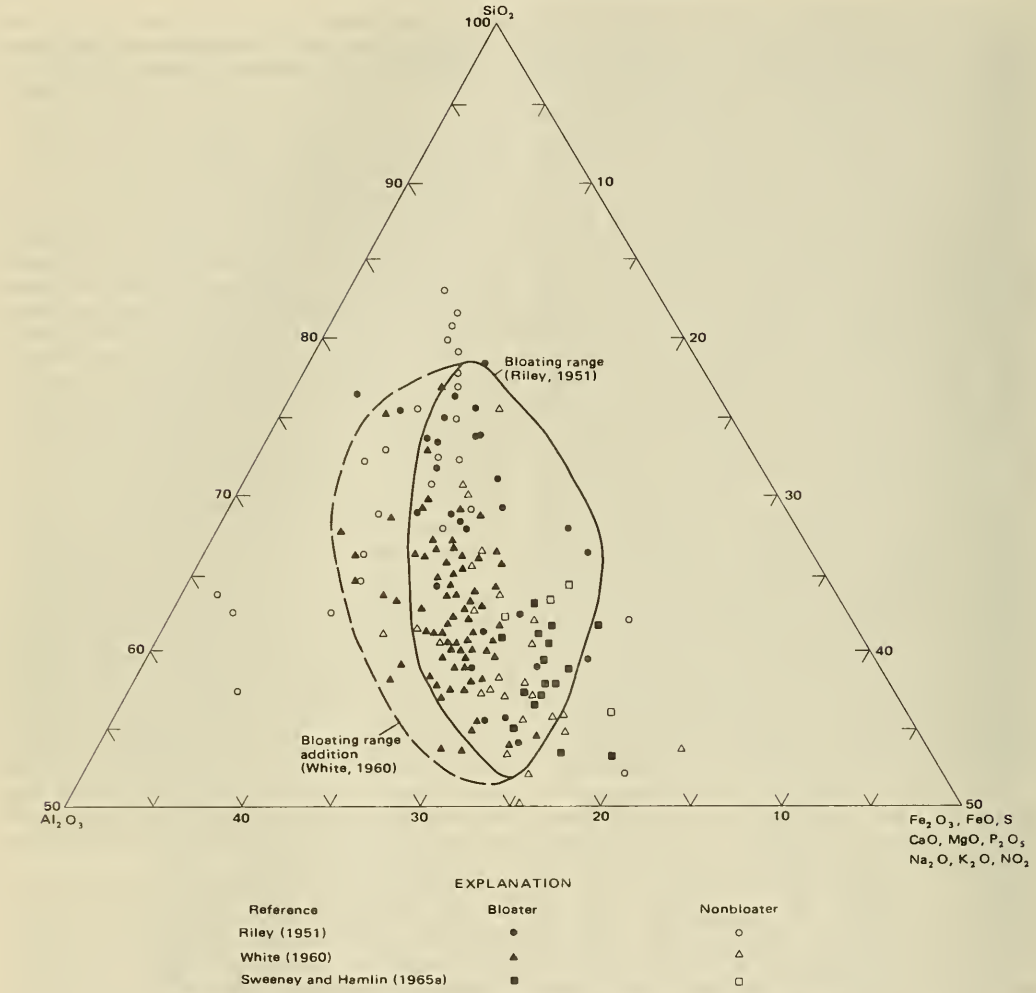

FIGURE 41.—Comparative composition of bloating and nonbloating argillaceous rocks.

the continental United States. The list of suitable rocks in the Appalachian region as given by Bush and Sweeney (1968) illustrates the number and variety available and is probably not complete.

The sheer volume of suitable rocks make reserve and resource problems somewhat different from those for most mineral commodities. The distinctions among proved, probable, and possible reserves are somewhat blurred, inasmuch as the principles of stratigraphic continuity allow for projection of the favorable unit for unusually great distances beyond points of observation, but the amount of accuracy in the calculation of tonnage is fair. In most mineral deposits, paramarginal and submarginal reserves are in lower grade, larger tonnage masses for which a complex interplay of costs determines profitability. In this situation the entire rock mass is the ore, changes in processing technology are seldom involved, and transportation costs are usually the determining element in separating recoverable, paramarginal, and submarginal reserves. The distinction between hypothetical and speculative re-

sources is similarly blurred, for the concept of deposits in mining districts really does not apply to the distribution of argillaceous rocks throughout the United States. Geologic mapping in the United States, at scales adequate to identify the presence of argillaceous rocks, is sufficiently complete to virtually rule out the possibility of finding additional units. What remains to be found are those deposits that would be classed as submarginal or, at best, as paramarginal.

Reserves of expandable clays, shales, and slates are so large that they can be relied upon to satisfy the Nation's needs for many years. If those needs are projected from 1970 through 2000, starting with the estimated actual 1970 production of slightly more than 10 million tons and projecting an annual growth rate of 5 percent, the cumulative production is about 670 million tons. That figure, though impressive, is seen in better perspective if it is allocated among the 36 States that produced lightweight aggregates in 1970—an average per State of about 18½ million tons, or the mining of about 13 standard mining claims to a depth of a little less than 20 feet. Put another way, cumulative production through the year 2000 will represent about one-millionth of the tonnage of argillaceous rocks in the 48 contiguous States to a depth of 20 feet below the surface.

For a number of reasons the sum of recoverable reserves cannot be stated with much accuracy, but a reasonable estimate can still be made, based on other than strictly geologic reasoning. Between 70 and 85 processing plants (both kiln and sinter) have been in operation annually over the period 1965–70. Plant investments are large, ranging from several hundred thousand dollars to more than $1 million. Average annual production in 1970 was about 150,000 tons. Plant amortization requirements over about a 10-year period suggest the need for an average raw-material reserve of about 1.5 million tons per plant, about the equivalent of a standard-size mining claim quarried to a depth of 20 feet. In view of the stratigraphic characteristics of the argillaceous rocks, this is a very plausible estimate for almost any of the processing sites. As a rule of thumb, roughly equal amounts can be assigned to the proved, probable, and possible reserves, perhaps about 115 million tons each, or a rounded total of recoverable reserves in the presently known deposits of about 350 million tons. The sum of all reserves plus hypothetical and speculative resources is many times that of the recoverable reserves.

VOLCANIC ROCKS

Various volcanic rocks are suitable for use as lightweight aggregates; all are glasses, and they range in composition from mafic to silicic. Scoria, volcanic cinder, pumice, and pumicite make moderate- to low-strength structural aggregates, whereas expanded perlite and expanded pumicite are ultralightweight materials. The chemical composition of the glasses (table 68) faithfully mirrors that of

TABLE 68.—*Comparative composition of volcanic glasses*

[Tr., trace; ND, not determined; NA not applicable]

Sample	Pumicite				Pumice				Perlite			Obsidian			Scoria	
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
SiO_2	73.32	71.98	68.43	72.3	60.10	67.50	69.47	70.38	73.20	67.06	72.75	74.41	73.38	72.93	50.90	44.6
Al_2O_3	10.76	10.94	12.94	11.8	13.66	12.96	13.48	15.82	12.17	14.31	13.34	13.33	13.69	15.53	18.24	24.5
Fe_2O_3	1.66	1.93	1.22	1.7	3.30	2.32	1.43	1.50	.75	.92	1.12	.08	1.84	1.20	7.77	8.3
FeO	----	----	----	----	----	----	----	1.42	.30	1.48	[1].89	.85	.13	----	----	----
TiO_2	1.36	.33	----	.5	Tr.	.50	.25	----	.13	.34	[2].13	.05	.12	----	1.79	----
CaO	.53	2.14	1.17	1.0	4.96	1.06	1.13	1.66	1.08	2.44	1.13	1.90	1.38	1.31	9.58	6.4
MgO	.23	.16	.22	.3	.72	.01	.20	.48	.13	.66	[3].19	.43	.37	.18	5.73	2.0
K_2O	5.30	5.94	2.16	[4]5.4	.68	2.41	1.70	4.10	5.16	3.94	[5]4.22	4.30	4.22	3.87	2.20	5.2
Na_2O	2.27	2.08	3.60	[4]2.7	2.00	9.89	6.58	3.70	3.12	4.16	[5]3.01	2.99	3.92	3.47	4.90	8.6
P_2O_5	Tr.	Tr.	----	----	ND	----	----	----	.02	.12	.08	.23	.08	----	----	----
SO_3, SO_4, S	ND	0	----	----	[6]1.83	[7].12	[7].08	----	----	----	----	----	[8].03	----	----	----
MnO	----	----	----	----	.14	----	----	----	.08	Tr.	----	.05	.02	----	----	----
Other	----	----	[9].78	----	----	----	----	----	----	----	----	----	[10].12	----	----	----
Loss on ignition (also total H_2O)	3.93	4.51	9.81	4.3	12.87	3.17	5.60	3.62	3.62	4.85	4.03	.52	.39	.36	.93	.3
Total	99.36	100.00	100.22	NA	100.16	99.94	99.92	102.58	99.76	99.95	NA	99.15	99.69	NA	102.04	NA

[1] Average of four analyses.
[2] Average of 14 analyses.
[3] Average of 15 analyses.
[4] Average of 40 analyses.
[5] Average of 20 analyses.
[6] SO_3.
[7] SO_4.
[8] S.
[9] CO_2, 0.31; Cl, 0.47.
[10] Cl.

SAMPLE LOCATIONS AND REFERENCES

1. Sample JV–6, Pearlette ash, Kansas (Carey and others, 1952).
2. Sample NNV–1B, Calvert Ash Bed of Ogallala Formation, Kansas (Carey and others, 1952).
3. Pumicite at Shoshone, Calif. (Chesterman, 1956).
4. Average of 54 analyses, Kansas (Bauleke, 1962).
5. Mono County, Calif. (Chesterman, 1966).
6. Italy (Talmage and Wooton, 1937).
7. Mount Taylor, N. Mex. (Talmage and Wotton, 1937).
8. Average of 80 analyses (King, 1948).
9. Socorro deposit, New Mexico (Weber, 1963).
10. Deschutes deposit, Oregon (King, 1948).
11. Average of 21 analyses: 11 from King (1948); 10 from Anderson, Selvig, Baur, Colbassani, and Bank (1956).
12. Shirataki, Japan (Yagi, 1966).
13. Glass Mountain, Calif. (Chesterman, 1966).
14. Average of three analyses, Oregon and California (King, 1948).
15. Red Cinder Mountain, Calif. (Chesterman, 1966).
16. Average of six analyses, Idaho (Asher, 1965).

their crystalline counterparts; scoria and cinder are like basalts (and basaltic andesites), and pumice, pumicite, and perlite are like granites and rhyolites. Contained water in basalts is little different from that in scoria and cinder, but the difference between that in the granitic rocks and that in silicic glassy rocks is significant. It is this excess of water that allows the perlites and pumicites to be thermally expanded. In a general way, the viscosity of the extruded rock melt varies directly with the SiO_2, Na_2O, and K_2O content and inversely with the Fe_2O_3, FeO, CaO, and MgO content; thus, whereas the mafic rocks are more fluid, the silicic rocks are more likely to retain gases.

SCORIA AND VOLCANIC CINDER

Scoria and volcanic cinder are cellular, frothy products of explosive volcanism—erupted as tephra (blocks, bombs, lapilli, and gravel) or lava flows from mafic magmas. Much of the material is forcefully ejected from the vent, vesiculating in the air as the volcanic gases (mostly water) expand and are entrapped by the rapid cooling of the relatively fluid lava. Scoria also develops where the gases are entrapped by rapid cooling at the surface of the flows; it may then be broken into blocks and irregular fragments by continued movement of the flows. There is a fairly wide range in vesicle size (particularly in the ejecta, most of which have dense fused surfaces) and in the thickness of the cell walls, which results in a considerable variation in the density of the rocks. The distinction between scoria and volcanic cinder is an arbitrary one of size; cinder is the material less than 1 inch (about 2.5 cm) in largest dimension. Characteristically, mafic ejecta are fairly heavy and are not thrown long distances from the vent; they form cinder cones around the vent that are generally a few thousand to several thousand feet in diameter and several hundred feet in height. In contrast, mafic lava flows (basalt or basaltic andesite) tend to be fluid, several hundred feet to tens of miles in lateral extent, and a few feet to several tens of feet thick. The flows are seldom abundantly scoriaceous throughout; most of vesicular zones are confined to the upper few feet of the flow and are highly variable in their development.

Most of the deposits of scoria and volcanic cinder are geologically youthful, in Quaternary or upper Tertiary terranes (<1–11 m.y. old), and some are only a few thousand years old. Many mafic extrusive rocks are latecomers in the volcanic sequence and, thus, are less likely to be buried deeply enough to survive prolonged erosion. In addition, the ejecta seldom make well-consolidated resistant lithologic units because the individual blocks, bombs, and lapilli do not weld together consistently. They are easily eroded and, in humid climates, are subject to rapid chemical weathering. Although the ejecta enter readily into the sedimentary cycle, they are not persistent in it. They lack sufficient resistance to abrasion to survive reworking for very long in the moderate-energy environment needed to move them to protected sites where they can be preserved.

Mafic vesicular volcanic rocks are widely distributed throughout the Western United States, including Hawaii and Alaska, but are missing from the Central and Eastern States. Deposits of scoria and cinder are known in every State west of the 104th meridian, and production was recorded in 1969 or 1970 from all States but Alaska. Arizona, Oregon, California, Hawaii, and New Mexico are the largest producers, generally in that order; however, in 1970 Oregon was first. The ranking in production does not always reflect the relative amounts of scoria and cinder available, in part because production is determined by competition and the size of the market within economic range of the deposits and in part because the reporting of production includes pumice and pumicite. In the States west of 104°, nearly all the metropolitan districts with a core city of at least 50,000 people and most cities of at least 25,000 are within about 100 miles of deposits of scoria or cinder, but not all can be served economically from them.

Estimating the recoverable reserves of scoria and cinder is an exercise in very short term prediction, for production is extremely sensitive to the state of the construction industry, and pits can be and are shut down quickly. For example, Meisinger (1972) reported the closing in 1970 of 48 operations of the 171 that were open in 1969. His figures are for all pumice, pumicite, scoria and cinder operations, but inasmuch as 85 percent of the total production was cinder, it seems reasonable to assume that most of the closed operations were also for scoria or cinder. Although the more than 25 percent drop in operations resulted in only a 15 percent drop in output from 1969, it might represent either a larger or smaller decrease from the 1969 recoverable reserves, for when an operation closes, all its recoverable reserves, by definition, become at least paramarginal.

For scoria and cinder, the economic criteria that separate recoverable from paramarginal and submarginal reserves are primarily the level of activity of the construction industry and competition from expanded clays, shales, and slates. Other materials,

like expanded slag and fly ash, are not significant competitors in the Western States. The stumbling block is usually the cost of transportation, and this cost almost invariably cannot be decreased. For most commodities the grade of the ore enters into the criteria, and new techniques of recovery may convert protore into ore. These criteria are not particularly applicable to any of the nonmetallic deposits, where the whole rock mass is the ore. Volcanic ejecta have already undergone a crude form of aerial classification that has substantially separated vesiculated from dense rock. Only a small additional tonnage could be won at any deposit by separating vesiculated rock from predominantly dense rock. In deposits that are scoriaceous zones in flowrock, more intermingling of vesiculated and dense rock occurs, but even here the additional tonnage to be gained is small, and the cost of winning it comparatively high. In summary, these paramarginal resources are not significant.

An order of magnitude can be established, although not from strictly geologic evidence, for both the recoverable reserves and the identified resources. For example, many cinder cones have basal diameters greater than 2,000 feet, and angles of slope (determined by the angle of repose for fragmental volcanic material) that range from 30° to 40° (Colton, 1964). For a cone that has a 2,000-foot base diameter, a crater lip 425 feet above the base, and a crater 500 feet in diameter at the lip, the angle of slope is less than 30°, well within the angle of repose. Depending on the density of the scoria, which can range from 1,000 to 1,500 lb per cu yd (pounds per cubic yard), such a cone could contain from 10 to 15 million tons. One such cone, then, can contain from three to six times the entire U.S. production of volcanic cinder, 2,656,000 tons for 1970 (Meisinger, 1972, p. 965). An assumption seems reasonable that 25–30 of the operating pits in 1970 (there were more than 100 in all) were in cinder cones of this size in the 10 or more States where scoria was produced; as a result, recoverable reserves that year were between 250 and 450 million tons in just those deposits. In the category of paramarginal resources, economically recoverable at 1.5 times the present price (McKelvey, 1972), there are probably a similar number of deposits and tonnages and, also, a similar quantity in the submarginal resources. Identified resources can be thought of as 1 billion tons, plus or minus 25 percent.

Let us put it in another kind of perspective. If we assume that 3 million tons of scoria and cinder was produced in 1970 and that an annual growth rate of 5 percent persists through the year 2000, we shall have need for a cumulative output of about 200 million tons. That appears to be significantly less than the recoverable reserves in the cinder cones being mined in 1970.

The category of hypothetical resources requires a different approach, for basically the search is not for hidden deposits but for unmapped ones. By 1972 the location of most of the cinder cones and mafic lava flows in the conterminous United States probably had been depicted on some sort of geologic map at some kind of scale. Knowledge of the sizes and volumes of these cones and flows and of the ratio of vesicular to dense rock within them is what is required to convert their status to one of the reserve classes. The distribution of the deposits that make up the identified resources suggests that there may be at least an equal number for which information on size is lacking, and, on that basis, the hypothetical resources can be estimated to be on the order of 1 billion tons, as well.

Speculative resources require a further exercise of the imagination. Higgs (1949) estimated that Cenozoic extrusive rocks in the conterminous United States covered 8.368 percent of the land surface. In the absence of other estimates on the ratio of mafic to silicic extrusives at the surface, and for ease of estimation, let us assume that mafic rocks cover only 1 percent of the surface and that they average about 50 feet thick. Let us further assume that 1 percent of this volume is scoriaceous. This is equivalent to about 3 cubic miles of scoria, or about 9 billion tons. The potential reserves and hypothetical resources listed above can be adequately accommodated within this total resource.

PUMICE AND PUMICITE

Pumice and pumicite are the silicic extrusive equivalents of scoria and volcanic cinder but are lighter in color, of lower density, and more highly cellulated. In pumice the voids may be spherical, ovoid, tubular or irregular; the cell walls are commonly very thin; and the rock is light enough to float. If sufficient gas and steam are available during explosive extrusion, the pumiceous froth is very commonly shattered, and the shards and finer fragments form pumicite (volcanic ash). The range in composition (table 68) is from rhyolitic to dacitic, andesitic, and even basaltic, but most pumices are in the rhyolite-dacite range. The higher viscosity of the silicic rock melts generally leads to more violent extrusion, and the lower density pumice and pumicite are thrown much farther from the vents than the scoria and cinder; many pumicite deposits are several hundred miles from their sources.

Deposits of pumice and pumicite occur in a larger variety of forms than do scoria and cinder. A very common form is an air-fall blanket, semiconcentric to a crater source vent or broadly fan-shaped lateral to fissure vents and more extensively developed along the prevailing wind directions. Pumice cones along fissure vents are also numerous. Very large volumes occur in ash-flow tuffs and in the upper parts of rhyolite and "obsidian" domes. Any of these deposits is subject to rapid erosion, reworking, and consequent redeposition as stream or lake sediments. Thicknesses range from a tenth of an inch to many tens of feet, and areal extents range from a few square feet to tens of square miles; therefore, volumes may be a few tons or many hundred thousand tons. Ash-fall deposits are more likely to be interbedded with other sediments than are ash flows, and reworked and redeposited materials very commonly are interbedded.

In contrast with ash falls, most ash flows are unsorted, heterogeneous mixtures of pumice and ash, the pumice occurring in fragments and blocks as much as perhaps 8 or 10 feet in maximum dimension. Commonly, ash flows were hot enough and cooled slowly enough to weld and to cause the pumice to soften to the point of collapse, so that dense glassy zones in the central or lower part of the flow were formed. Ash flows are crudely sorted, with most of the larger blocks and fragments close to the source and successively finer materials at greater distances; the finest ash may be carried for hundreds of miles. Some ash falls also retained enough heat to weld and to form glassy zones. Where ash and pumice fall directly on standing bodies of water, and where reworked material is deposited in quiet water, an inverted graded bedding may occur. The finest material has the greatest density and settles first, whereas coarser material is vesicular, floats longer, and is deposited last.

Pumice deposits occur in all the Western States from the Rocky Mountains to the Pacific Ocean, and pumicite deposits are in Texas, Oklahoma, Kansas, North and South Dakota, and Nebraska nearly as far east as the Missouri River. In 1970 pumice or pumicite was produced in every Western State but Montana, and in Hawaii as well. Oregon and California were probably the leading producers of pumice, and Kansas was the leader in pumicite. Production statistics are so grouped that accurate data for each rock type cannot be determined.

Prediction of the resources base for pumice and pumicite presents many of the same problems as for scoria and volcanic cinder. Any figure for recoverable reserves reflects wide annual variations in the number of operating mines and no accurate census has ever been kept of producers grouped by product. In part, the extreme increases and decreases in annual tonnage (fig. 40) reflect this imprecise classification, but they also suggest that many of the operations were marginal and that what were recoverable reserves one day were paramarginal the next. Since 1957, except for 1963 and 1964, the overall trend has been toward smaller production. But because most pumice and pumicite is used in the construction industry, the long-term-consumption trend will be a growth rate similar to that for construction. On the basis of the 1960–70 average annual output of slightly more than 600,000 tons and the previously used annual growth rate of 5 percent, cumulative production through the year 2000 will be about 40 million tons.

Recoverable reserves can be estimated only within very broad limits. In 1970 some 30 mines operated in the conterminous United States. Although the range in deposit size seems to be fairly large, a conservative estimate suggests that many occurrences have dimensions of 500 by 1,000 by 10 feet. Bulk densities range from 850 lb per cu yd for pumice to 1,750 lb per cu yd for pumicite; tonnage for the sample deposit lies between about 80,000 and 160,000 tons. Thus, the 1970 level of operations might entail between 2½ and 5 million tons of rock as recoverable reserves, ignoring all past production. Estimating paramarginal and submarginal resources each at twice the recoverable reserves is acceptable (see estimate of the total resource below) so that the identified resources can be thought of as a minimum of 25 million tons, more than half the amount needed through the year 2000.

The total resource can be approximated on the same basis as that for scoria and volcanic cinder, using Higgs' (1949) estimate (8.368 percent) of extrusive rocks at land surface in the Western States. Higgs' method excludes all volcanic ash in the States east of the Rocky Mountains, however. Again no reliable estimates of the relative amounts of silicic, intermediate, and mafic volcanic rocks are available, but a general feeling among geologists indicates that intermediate rocks predominated in the early and middle Cenozoic and that both silicic and mafic rocks were abundant in the late Cenozoic, the mafiic rocks possibly having been more abundant. Basic rocks were assumed to occupy 1 percent of the surface for the scoria estimate; here, let us assume 0.1 percent coverage and an average thickness of 10 feet for the silicic rocks; let us further assume that 1 percent of this volume is pumice or pumicite. These parameters would seem to be almost

minimal. On the basis of these assumptions the total resource is between 150 and 300 million tons, exclusive of the volcanic ash of the Great Plains.

Pumicite deposits on the Great Plains are numerous and vary greatly in size; Ham (1949) reported one in Oklahoma to contain about 10 million cubic yards (perhaps 7–8 million tons). He estimated a total of about 20 million cubic yards in known deposits; by our definitions this 20 million cubic yards would be considered an identified resource of about 17–18 million tons. Carey, Frye, Plummer, and Swineford (1952) estimated about 20 million tons for known deposits in Kansas, which we would also class as identified resources. Data are lacking for Nebraska, but on the basis of past production and the distribution of the deposits, a tonnage on the same order of magnitude as Kansas and Oklahoma is reasonable. A conservative estimate for all the Great Plains States may be taken as 50–60 million tons of identified resources, and perhaps the same amount for hypothetical and speculative resources combined; the total resource may be thought of as about 100–150 million tons.

DIATOMITE

Although diatomite has been and is used as a lightweight aggregate, the usage seldom exceeds a few tens of thousands of tons per year and is not a significant factor in the reserve and resource position of the United States. In general, its value for other uses, such as filter aids, is far too great to justify its utilization as a low-cost aggregate. Only in a very few special cases can diatomite be used economically, and then it is generally as a byproduct from the treatment of the material for its more specialized roles. Information on distribution, geologic habit, and resources are in the chapter "Diatomite."

OTHER MATERIALS

Expanded blast-furnace slag and fly ash are a significant part of the supply of structural lightweight aggregates in the heavily industrialized Great Lakes and Pennsylvania areas and in Alabama, Colorado, California, and North Carolina. Expanded slag production ranged from about 2½ million tons per year during the period 1960–70 (fig. 40). Expanded slag is only a fraction of the slag produced annually; it is likely to be ample to meet any demand for many years. Fly ash production (which includes bottom ash) in 1970 was more than 35 million tons and was widely distributed throughout the country with only about 4 million tons being utilized in any way. Lightweight aggregate production of sintered fly ash totaled about 260,000 tons and was confined to the Detroit, Mich., Pittsburgh, Pa., and Charlotte, N.C., areas.

There appears to be an obvious market potential for both expanded slag and fly ash—perhaps a little more favorable for the ash—because the coal-burning power-generating stations are widely distributed and the country's increasing demands for energy probably entail the construction of more plants.

ULTRALIGHTWEIGHT AGGREGATES

INTRODUCTION

The natural ultralightweight aggregates are perlite, pumicite, and vermiculite; the first two are products of dominantly silicic volcanism (see section on "Pumice and Pumicite"), whereas vermiculite is a low-temperature alteration product of ultramafic igneous and metamorphic rocks. High-temperature heating is required of all three crude ores to cause expansion and to develop the vesicularity that gives the materials their desirable attributes. Properly treated, all three materials develop high porosity but low permeability and have very thin cell walls. Thus, they make excellent thermal and acoustic insulators, but their compressive strength is low. Concretes and plasters using them as aggregates have strengths from 100 psi to about 2,200 psi; the more cement used, the greater the strength and the greater the weight. The materials are very well employed in fireproof plasters, in concrete curtain walls, floor fills, and roof decks, in concrete refractory and insulating walls in bake ovens, and in decorative, non-load-bearing blocks and facings (Schroeder, 1970a, b). In loose fill or bulk form they are primarily used for insulation, both thermal and acoustic, but significant amounts are used as inert carriers and extenders in horticultural products and in manufacturing processes.

As with the structural lightweight aggregates, the ultralightweights are not indispensable; synthetic materials (polystyrene beads, polyurethane foams, foamed phenolic resins) can be substituted in some applications; lightweight concretes and plasters can be made by air entrapment through the use of aluminous foaming compounds; foamed glass can be used for some special requirements. In general, however, the use of expanded natural materials is more economic and less complicated in preparation and use.

The United States produces all the perlite and pumicite that it consumes and has ample material to export, but, because of the low unit value of crude perlite, only a few thousand tons is exported annually—all of it to expanders in Canada. No

pumicite is exported. Almost all the vermiculite used in the United States is produced domestically, but along the eastern seaboard, oceanic freight rates allow some vermiculite to be imported economically from the Republic of South Africa. In 1970 the United States was the world's largest producer of crude vermiculite, at about 285,000 tons, and South Africa was second, with about 134,000 tons (Fulkerson, 1972). The most recent import data are for 1969, when about 6,500 tons entered the United States; this was equivalent to a little more than 2 percent of the domestic production.

EXPLOITATION

The production histories of vermiculite and perlite are broadly similar in their early periods, and are very closely related since about 1955 (fig. 42). Vermiculite was first produced in Colorado in 1913, but the first significant sustained production began in Montana in 1925, with about 100 tons of crude ore. The growth rate was rapid, but the tonnages were small to 1937 (about 27,000 tons in 1937). The rate then became more gradual, but tonnage increased to about 200,000 tons in 1950, and then growth was slow but steady to about 300,000 tons in 1969 and 1970. Perlite production began after World War II and about 5,000 tons of crude ore was produced in 1946; output rose rapidly to about 150,000 tons in 1951, and growth has continued at a slower but steady rate to more than 450,000 tons in 1969 and 1970. Since 1955 the annual increases and decreases in production of crude vermiculite and crude perlite virtually parallel each other, with the production of perlite about 150,000 tons greater than that of vermiculite. Consumption of expanded perlite has varied more than that of exfoliated ver-

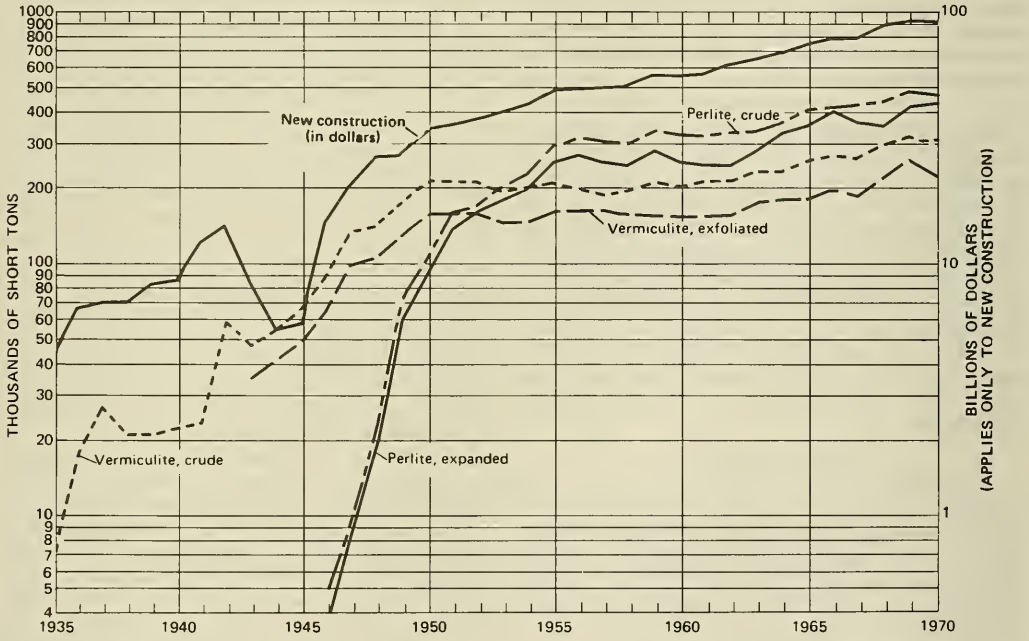

FIGURE 42.—Production of materials used as ultralightweight aggregates in the United States, 1935–70; U.S. Bureau of Mines Minerals Yearbooks.

New construction.—Value of total new construction, exclusive of maintenance and repair; data from Statistical Abstracts of the United States, 1935–70.
Perlite, crude.—Total crude ore sold and used by producers.
Perlite, expanded.—Total produced.
Vermiculite, crude—Total crude ore sold and used by producers.
Vermiculite, exfoliated.—Total produced.

miculite, in part reflecting the dominance of the vermiculite market by a single company, and in part reflecting the movement of perlite into the filter-aids field at the same time as a decrease in perlite use in concretes and plasters.

Perlite, pumicite, and vermiculite share the common problems of open-cast mining, but because many of the deposits are located in remote or sparsely populated areas, public concern with the mining operations has been minimal to date (1972). That is not true of the processing plants. Large amounts of fines are produced in the grinding circuits in the processing of perlite, and additional amounts are produced in the explosive expansion ("popping") of perlite and pumicite. Their disposal is a problem from several aspects. Because both materials are glasses, the fines are pointed, sharp slivers and shards. Dust control is a major problem, both in preventing and alleviating pollution beyond the limits of the plant itself and in protecting plant workers from respiratory injuries and diseases. These problems are not so severe for vermiculite, which yields thin flakes to the fines; where wet classification methods are used, the disposal of vermiculite slimes presents other difficulties.

VOLCANIC ROCKS

PERLITE

Obsidian, perlite, and pitchstone are volcanic glasses of generally silicic composition and are the equivalents of rhyolites, rhyodacites, trachytes, or latites. Among themselves, they differ chemically primarily in water content; obsidian has no more than 2 percent H_2O, perlite has 2–5 percent, and pitchstone has more than 5 percent. The general range of composition (table 68) is SiO_2 from 70 to 75 percent and Al_2O_3 from about 10 to 15 percent. The water content seems to be the only chemical component critical to expansion, and even then obsidians with as little as 0.2 percent H_2O are reported to have expanded satisfactorily (King, 1948). Originally, perlite meant a glassy rock characterized by concentric cracks, the "perl" (from the German "Perlstein") referring either to the resemblance of broken-out fragments to pearls or to the pearly luster of the surfaces. Today's commercial usage includes any glassy rock (except pumicite), regardless of composition or origin, that can be made to expand by heating to about 2,000°F (1,100°C). Most commercial perlites fit the petrographic definition that emphasizes a 2- to 5-percent water content.

Many of the traditional applications of perlite are in the construction field, but an increasing percentage of the annual production over the past several years has gone into filter aids (1964, 15 percent; 1970, 23 percent). Diatomite is the principal material used in filtration, but perlite seems to be making significant inroads into the market. In the construction field the principal competition comes from exfoliated vermiculite; in 1970 some 200,000 tons of perlite and 180,000 tons of vermiculite were used. Schroeder (1970a) gave a rather detailed discussion of perlite processing, marketing, uses, and substitutes.

Perlite is found in three major associations; in glassy zones in welded ash-flow tuffs, in lava flows from volcanic domes, and in the wall zones of felsitic intrusive plugs and dikes. Smith (1960) has described the central zone of dense welding in a simple cooling unit of an ash flow as a glass with virtually no porosity, composed of completely collapsed pumice and ash, and bordered successively, both above and below, by a zone of partial welding and a zone of no welding. Sparse phenocrysts of feldspar, quartz, biotite, and hornblende may be present in all the zones. Ash flows may be deposited before cooling of an underlying one has proceeded very far; as a result, composite cooling units may result. In these, the zones of dense welding may coalesce, and the intermediate zones of partial welding and no welding are obliterated. In such a stack of flows, very thick densely welded zones of glass can develop. Characteristically, the welded zones pass laterally into zones of devitrification toward the central area of the cooling unit; thus, a zone of glass borders and envelops a zone of felsitic tuff. However, if cooling is sufficiently rapid to prevent crystallization, the glass may be preserved for some millions of year. Preservation of glasses, regardless of origin, is increasingly rare from the Pliocene back to the beginning of the Tertiary and is very rare in rocks older than that.

The glass that develops in flows and in volcanic domes represents the rapidly cooled lava liquid, rather than collapsed pumice. Glass develops near the surface of the flow or dome and may be rolled under as the flow advances. In the process it may be brecciated, remelted, and annealed. As the flow comes to a stop, a zone of glass can be near its surface and near its base, and if cooling is rapid enough the zones may coalesce to make a flow that is virtually all glass. As with the ash-flow units, the glass may pass laterally into a felsitic central zone. In a somewhat analogous manner, a selvage of rapidly chilled glass can be formed at the con-

tact of a dike or plug with the country rock; in this type of occurrence the glass apparently devitrifies most rapidly.

Perlite very commonly surrounds cores of obsidian, and there is a full range of occurrences from obsidian containing a minor amount of perlite along a network of fractures, through nearly equal amounts of perlite and obsidian, to complete perlite. Most obsidian cores range from about 1 inch in diameter to microscopic. Ross and Smith (1955) discovered a very marked, abrupt contrast in water content between the obsidian cores (a few tenths of 1 percent) and the surrounding perlite (2–5 percent). They attributed the contrast to hydration of the glass after emplacement, on the basis of marked differences in the indices of refraction between obsidian and perlite and the relative ease of dehydration of perlite below 600°C as compared with dehydration of obsidian between 800° and 1,000°C. They suggested that the water in obsidian was pristine and that the water in perlite represented hydration from snow, rain, and ground water. Investigations of the deuterium content of the water in obsidian and perlite by Smith and Friedman (1957) and Friedman and Smith (1958) showed that most of the water in perlite was indeed of meteoric origin. These conclusions and the increasing devitrification of glass with increasing age are of importance to the consideration of perlite resources.

As with the other volcanic glasses, perlite is widely distributed throughout the western conterminous United States (Jaster, 1956). In 1970 the production of crude ore came from New Mexico (87 percent), Arizona, California, Nevada, Colorado, Idaho, and Utah. A very few deposits have had short-term production in Oregon and Texas; other deposits are known in Montana, Wyoming, and Washington.

Basic data on which to build a detailed estimate of the recoverable reserves of perlite in the United States are lacking. Simply, from the broad geologic knowledge of the very large volumes of extrusive rocks available, no shortage is foreseeable. As an example, some 600,000 tons of crude perlite was produced in 1970, and about 420,000 tons of expanded perlite was consumed, a ratio of about 1.5 tons of crude for 1 ton of expanded. The perlite industry is moving toward less dependence on the construction industry, and so an annual growth rate (6 percent) should be assumed that can take into account consumption in additional new, and perhaps more rapidly growing, fields. Through the year 2000, the cumulative need for crude perlite production will total about 48 million tons. Schilling (1960, p. 108) estimated that in north-central New Mexico alone "There is over 100 million tons—probably several hundred million tons—of readily minable, commercial-grade perlite in the No Agua deposit." This is the district which produced nearly all the perlite mined in 1970. Even if this estimate should be an order of magnitude too large, a single district can apparently furnish at least one-fourth of the anticipated demand.

Numerous sizable deposits also are present in California (Chesterman, 1957, 1966), Arizona, Nevada, and elsewhere in New Mexico, all with reserves that appear to be in millions or tens of millions of tons. Other large deposits, but fewer, are present in Colorado (Bush, 1951, 1964), Utah, and Idaho. No quantitative data are available to estimate the amounts of paramarginal and submarginal resources, but the paramarginal resources (determined more by costs of stripping and transportation than by lower expansibility or greater dilution) are likely of the same order of magnitude as the reserves, whereas the submarginal resources are considerably smaller. Using the same approach as for pumice and pumicite, the total resource can be approximated very conservatively at about 650 million tons.

The hydration of silicic volcanic glass by meteoric water raises the problem of how far the glasses are hydrated inward from their margins. The extent is surely a function of the thickness and permeability of the overlying rocks and of the structure, texture, and attitude of the host rocks. In the absence of data on the extent of hydration, any reserve or resources estimate must be considered to be a maximum.

PUMICITE

Laboratory investigations by the Oklahoma Geological Survey in 1944 revealed that pumicite was capable of considerable expansion upon heating in excess of 1,100°C (Burwell, 1949). Additional investigations by the Kansas Geological Survey in the 1960's provided many more data on temperatures and strengths and suggested industrial uses as filter aids and ultralightweight construction materials (Bauleke, 1962; Hardy and others, 1965). Discussion of geologic habit, reserves, and resources is given in the section on "Pumice and Pumicite."

VERMICULITE

In contrast with all the other naturally occurring lightweight aggregate materials, vermiculite is a single mineral rather than an assemblage of minerals. The rocks that are suitable for use as lightweight aggregates are abundant materials that oc-

cur in common geologic terranes, although they may not be ubiquitously distributed. The varieties of Cenozoic extrusive rocks previously described are good examples; they occur in a great many localites throughout the western conterminous United States. In searching for recoverable reserves of vermiculite, however, one must find a suitable host rock, then the site where it is in the proper geochemical environment, and then the specific areas where alteration has produced the mineral in the concentration needed to be useful. For vermiculite, the search must start with an understanding of the mineral and its origin.

Mineralogically, vermiculite is a micaceous, hydrated magnesium iron aluminum sheet silicate, of variable composition, composed of a basic unit formed of two tetrahedral silicate sheets which face each other and which are joined by an octahedral sheet that contains the aluminum and iron (Grim, 1962). This configuration is also the basic structural unit of a single mica layer; the micas are built up by a repetitive stack of these layers. Each layer, on its upper and lower surfaces, has regularly arranged "holes" that overlap corresponding sites on overlying layers. In biotite, potassium atoms occupy these sites, and their electronic charges help to hold the layers together. In vermiculite, only some of the sites are occupied, and these only by magnesium, but a double layer of water molecules also is present in these interlayer regions.

Commercially, "vermiculite" includes any micaceous mineral that is capable of expansion, regardless of its chemical composition or the regularity of its crystal structure. Pure vermiculite can be expanded (exfoliated) up to 30 times its original thickness when heated to about 1,600°–2,000°F (870°–1,100°C), impure varieties expand less. The exfoliation results from the flash conversion of the interlayer water molecules into steam; the mineral develops a high degree of porosity as the layers are forced apart into an accordionlike structure. The resulting material is easily compressed along the line of expansion, but it has moderate strength in other directions. Schroeder (1970b) has listed many of the uses of exfoliated vermiculite; most are connected with the construction industry, which in 1970 consumed more than 80 percent of the output, about equally divided between aggregates for concrete, cement, and plaster, and insulating uses, mostly as loose fill.

Vermiculite is an alteration product of a variety of mafic minerals; it has not been found as a primary rock constituent. The geologic literature has many descriptions of vermiculite derived from biotite, phlogopite, diopside, tremolite, augite, hornblende, olivine, chlorite, and serpentine. The alteration may have included an intermediate biotite or chlorite stage, for X-ray diffraction studies of the vermiculite reveal it to be interlayered with biotite or chlorite, although macroscopic and microscopic examination may show no biotite or chlorite elsewhere in the rock. Biotite is the common parent mineral, and the similarity of the biotite and vermiculite crystal structures permits an intimate interlayering on a molecular scale in a series that ideally extends either regularly or irregularly from pure biotite through 1:1 biotite-vermiculite to pure vermiculite. In a general way, varieties in the series from perhaps 10–50 percent vermiculite are called hydrobiotite. The alteration has been considered to be hydrothermal (Prindle and others, 1935; Leighton, 1954) or supergene (Murdock and Hunter, 1946; Roy and Romo, 1957; Bassett, 1959) and partly both (Boettcher, 1966). The character of the alteration has a major impact on the resources of vermiculite.

Almost all vermiculite deposits are associated with mafic and ultramafic rocks, both igneous and metamorphic, that have been intruded by silicic and in many instances by alkalic igneous rocks, and in some instances by carbonatites. They can be broadly grouped in three different types, but there are strong points of similarity among all the classes: (1) large ultramafic intrusives, such as pyroxenite plutons, sometimes zoned, that are cut by syenites or alkalic granites and by carbonitic rocks and pegmatites (examples are deposits at Libby, Mont., and Phalaborwa, Republic of South Africa); (2) small to large ultramafic intrusives, such as dunites and unzoned pyroxenites and peridotites, that are cut by pegmatites and syenitic or granitic intrusive rocks (examples are deposits in the Blue Ridge region of the Southeastern United States); and (3) ultramafic metamorphic rocks (usually amphibolite schists that commonly are layered) that may have originally been igneous rocks, sometimes cut by or in contact with pyroxenites or peridotites, and cut by pegmatites (examples are deposits in the Enoree district, South Carolina, and most of the deposits in Colorado, Wyoming, and Texas). With the major exception of the deposit at Libby, almost all the vermiculite deposits in the world appear to be in rocks of Precambrian age.

The world's largest vermiculite deposit at Libby, Mont., is a zoned pyroxenite pluton of middle Cretaceous age that cuts Precambrian sedimentary rocks of the Belt Supergroup (Boettcher, 1967)—a type 1 deposit. The pluton has a core of biotitite in a mass of biotite pyroxenite. A shell (like a ring

dike) of magnetite pyroxenite intruded the zone of weakness at the contact of the biotite pyroxenite with the country rocks. A younger mass of syenite cut both the magnetite and the biotite pyroxenite, and alkalic syenite dikes cut the biotitite core. Fenitized Belt rocks and a small nepheline syenite mass nearby suggest the presence of a carbonatitic mass at depth. Biotite in the biotite pyroxenite, and to a small extent in the magnetite pyroxenite, is altered to hydrobiotite and vermiculite; the biotite of the dense core is virtually unaltered.

Boettcher (1966) concluded that the hydrobiotite is the result of high-temperature alteration (presumably hydrothermal), whereas the vermiculite is the result of surficial alteration by circulating ground water. The evidence for hydrothermal alteration is not conclusive to me; a definite answer will probably not be gained until hydrobiotite is found below the level of ground-water circulation. A fairly intensive search of the literature has not turned up any such occurrences. The Mining Journal (1952) reported that vermiculite had been proved by drilling to a depth of 800 feet; as the deposit is located in mountainous terrain and underlies a ridge with from 800 to 1,200 feet of relief on three sides, it is very possible that the vermiculite from the bottom of the 800-foot hole was still in the zone of circulating ground water, the zone of surficial alteration. Many hundreds of thousands of tons of vermiculite have been produced from this deposit since mining began about 1925, and the deposit is far from depleted.

Vermiculite in the dunite-type (type 2) deposits of the Blue Ridge province also is found only in the zone of weathering. It occurs in veins and lenses along the commonly serpentinized contact of dunite and pyroxenite bodies with the metamorphic country rocks and with crosscutting pegmatites, and along fractures within the bodies. The largest deposits are at the contacts, but the highest concentrations are along the internal fractures. Where the country rock also is mafic (hornblende gneiss or biotite schist), the vermiculite may occur on both sides of the contact. In these deposits, vermiculite typically occurs in lenses that are as much as 4–5 feet thick and 50–60 feet long. A few lenses are 20 feet thick and more than 100 feet long (Hunter, 1950).

There is considerable variety among the deposits in the layered metamorphic rocks (type 3). Some of the amphibolite and biotite schists may have been sedimentary rocks, others intrusive or extrusive rocks, but all deposits are characterized by granitic or syenitic crosscutting pegmatites. The deposits in the second most important group in the United States are of this type, in the Enoree and Enoree-Waldrep districts of South Carolina, where many deposits have contained 20,000 to 50,000 tons of ore, and some as much as 100,000 tons of ore. In these districts, weathering is so intense that rock types are difficult to identify and the contact relations are very obscure. Hunter (1950) suggested that the vermiculite developed by deep weathering of biotite from lenses of pyroxenite in contact with biotite gneiss and schist. Only fragments of pyroxenite have been found in the deposits; the pyroxenite bodies may have been metamorphosed to amphibolite schists, which have been mapped in the Enoree area by McClure (1963). All the deposits are cut by stringers of pegmatite, and small masses of "granite" have been reported. Hunter (1950) described vermiculite lenses 450 feet long and 150 feet wide, with a depth to unaltered biotite of about 80 feet; these dimensions suggest pluglike bodies rather than dikes or layered rocks, but most of the deposits have length-width rations of 5:1 or greater—consistent with favorable zones in layered rocks.

The most numerous deposits, but also those with the smallest amounts of vermiculite, are in the layered metamorphic rock (type 3). Characteristically, the deposits are in biotite schists, amphibolite schists, or mica-amphibolite schists, and are cut by pegmatites. The deposits are only a few feet thick, although they may be several hundred long, and the depth of weathering is usually no more than a few tens of feet. Ore content usually ranges from a few hundred tons to several thousand tons. Hagner (1944) described several deposits of this type in Wyoming, and Clabaugh and Barnes (1959) did so for Texas. Descriptions of deposits in other States are given in publications listed in "Selected References."

In general, the geologic relations of all the types of deposits suggest that pyroxenes (diopside and augite), amphiboles (hornblende and tremolite), and olivine in the ultramafic rocks were altered by solutions and volatiles from intrusive syenites, carbonatites, and pegmatites (supplying mostly OH); and biotite, phlogopite, serpentine, and chlorite were formed. Supergene alteration by circulating ground waters later removed the alkalis, redistributed magnesium, and added H_2O as interlayer water molecules to form vermiculite. The position of 1:1 regularly interstratified hydrobiotite in the sequence is not certain (Boettcher, 1966), but I believe that it, too, is a supergene alteration product.

In order of significance, the vermiculite deposits of the United States are in Montana (almost two-thirds of the United States production), the Inner

Piedmont province of South Carolina (one-third of the production), the Blue Ridge province in Virginia, North Carolina, South Carolina, and Georgia, and scattered deposits in Wyoming, Texas, Colorado, California, Nevada, Arizona, Washington, and Oregon. The almost invariable association of vermiculite with Precambrian rocks allows Hawaii and virtually all the central part of the country from the Rocky Mountains east to the Blue Ridge to be dismissed from consideration, except possibly the Wichita Mountains and the Ozark Mountains.

All the recoverable reserves of vermiculite in the United States are in one deposit in Montana and in several deposits in the Enoree and Enoree-Waldrep districts of South Carolina. Inasmuch as almost all of them are controlled by a single company, and the rest by two other companies, it is not appropriate to publish a quantitative estimate. However, in 1952 a mining publication in London (Mining Jour., 1952) estimated that reserves at the Libby deposit ranged from 25 to 100 million tons. No grade was given, so the amount of vermiculite mineral that was available is uncertain. As a measure of the United States position, we can again estimate the cumulative output needed to satisfy the demand through the year 2000, using a 5-percent rate for the annual growth. Based on the 1970 production (Fulkerson, 1972) of about 285,000 tons of crude and 220,000 tons of exfoliated vermiculite, about 19 million tons of crude will be required. Since 1952 about 4.3 million tons of crude has been produced from all U.S. deposits. The total is less than the smaller estimate for the Libby deposit as published in 1952.

The remainder of the identified resources of vermiculite must be classed as submarginal, for it is unlikely that any of the other known deposits can be brought into operation at 1.5 times the present price. They are too small, or too low grade, or too poorly located to be able to compete at that price; thus, they cannot be considered paramarginal reserves. The total tonnage that can be estimated as submarginal reserves is on the order of 2–3 million tons in North and South Carolina, Texas, Wyoming, Colorado, and Nevada.

Hypothetical resources in the known districts are probably on the order of 1½–2 million tons—it is unlikely that a new Libby will be found in the known districts, but discovery of new deposits of the Enoree type can be expected. It is also unlikely that there is only one Libby deposit in the conterminous United States, and so a projection of 25 to 100 million tons in the classification of speculative resources seems reasonable.

Where and how are the hypothetical and speculative resources to be found? Most of the hypothetical resources, in deposits of the 20,000- to 100,000-ton size, are likely to come from deposits of the Enoree type in the Inner Piedmont region of South Carolina. Possibly a combination of airborne and ground geophysical surveys and detailed geologic mapping can locate these deposits. We should be able to distinguish the zones of ultramafic rocks from the granitic rocks by airborne magnetic surveys, and possibly we may be able to identify magnetic anomalies the size of the target vermiculite deposits. At present there are virtually no guides to favorable ground and ore deposits, other than the relationship to ultramafic rocks.

Deposits of the Libby size, which would contain most of the speculative resources, have geologic relations that are intriguing and encouraging for additional discoveries. The association of ultramafic plutons with syenites, alkalic rocks, and carbonatites is too common to be happenstance; the association of these rocks is known from several deposits in the United States (Rocky Boy, Mont.; Gem Park–McClure Mountain and Powderhorn, Colo.), in the U.S.S.R., and, in particular, in many parts of the African continent. Several generalized clues to places where these rocks may be found together are (1) the rocks are usually in Precambrian terranes, (2) they may be related to Precambrian structural trends, (3) they may exhibit significant magnetic anomalies, and (4) they may be characterized by ring-dike structures.

Several problems deserve investigation. What is the environment in which mafic minerals are altered to vermiculite? What are the temperature-pressure conditions and the role of solutions and volatiles from pegmatites, alkalic rocks, and carbonatites? What is the mineralogenic sequence—the need for formation of a micaceous mineral as an intermediate step between diospide and vermiculite, for example? What role does the composition of the ground water play in the formation of vermiculite, and what climatic factors affect the alteration, and in what way? In a broader context, where the answers are of importance to resources besides vermiculite, what are the guides to the localization of ultramafic rocks, of syenites and carbonatites and other alkalic rocks?

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LIMESTONE AND DOLOMITE

By Harold A. Hubbard and George E. Ericksen

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ABSTRACT OF CONCLUSIONS

Limestone and dolomite are at or near the earth's surface over at least 10 percent of the continental areas, and the resources are extremely large. However, high-purity stone suitable for chemical and metallurgical use is restricted in extent, but its resources are large, also. For uses in which physical properties of the rock are important, as in construction, many kinds of rock can be substituted for limestone and dolomite. For uses in which the chemical properties are important, substitutes are few, generally scarce, and more costly. Because limestone and dolomite are abundant, the price at the mine is low, and shipping costs constitute a major part of the price to the consumer. About two-thirds of the limestone and dolomite mined in the United States is used because of its physical properties, chiefly in construction as aggregate and fill and for related purposes, but a small amount is also used as an industrial filler. The remainder is used because of its chemical properties as a raw material in the production of portland cement, lime, alkali, calcium carbide, and glass; for flux in metallurgy; for agricultural purposes; and for a large number of minor purposes.

The largest resources of high-purity limestone and dolomite in the United States are in the central and eastern parts of the country, but details of the distribution of such stone are incompletely known. Consequently, some potentially valuable deposits are endangered by urban spread and by zoning regulations that restrict or prevent quarrying in populous areas.

INTRODUCTION

Limestone and dolomite, commonly referred to as carbonate rocks, are among the world's most widely used mineral commodities and are essential to modern industrial society. Huge quantities of these rocks are consumed annually in construction, in agriculture, and by the chemical and metallurgical industries. The total value of limestone and dolomite extracted annually is exceeded by that of only a few mineral commodities—sand and gravel, petroleum, and coal. Limestone and dolomite used for their physical properties, chiefly for construction purposes, occur in extremely large quantities on all the continents and constitute at least 10 percent of the near-surface rock of the continents. Large quantities of limestone are used in the manufacture of cement; the rock suitable for this purpose may be rather impure but is widespread and abundant, though less so than the limestone used in construction. High-calcium limestone and high-purity dolomite, which are needed for chemical and metallurgical purposes, are much less widespread and abun-

dant. Resources of these rocks are restricted to small parts of the continents. This chapter emphasizes limestone and dolomite that are used for their chemical properties; uses for construction are described in the chapter "Construction Stone." Magnesite, another carbonate rock, consists of the mineral magnesite, $MgCO_3$, and is used mostly as a refractory material. Magnesite is discussed in the chapter "Magnesian Refractories."

Distribution, characteristics, and uses of limestone and dolomite are discussed in many reports. The U.S. Bureau of Mines "Minerals Yearbooks" and "Mineral Facts and Problems" give information about production and use. Recent data about chemistry and technology are discussed in "Mineral Facts and Problems" (U.S. Bureau of Mines, 1970) and by Boynton (1967). New information about depositional environments and origin of limestone and dolomite—the result of intensive investigations during the last 20 years—aids the search for high-purity limestone and dolomite. Among recent reports giving such information are those in the symposia edited by Chilingar, Bissell, and Fairbridge (1967a), Friedman (1969), and Pray and Murray (1965). Summary information about the distribution of limestone and dolomite in the United States was presented by Gillson (1960, p. 148–183). Ericksen and Cox (1968) discussed distribution of carbonate rocks in the Appalachian region.

DEFINITIONS

Limestone and dolomite are rocks composed, respectively, of the minerals calcite, $CaCO_3$, and dolomite, $CaMg(CO_3)_2$; however, both limestone and dolomite commonly are called limestone by the industry, and intermediate varieties are not distinguished. Some newly deposited limestone consists chiefly of the mineral aragonite, which has the same composition as calcite but a different crystal structure. The aragonite structure is unstable, and with time aragonite gradually changes to calcite. Commonly, both calcite and dolomite occur in the same rock, but generally one predominates in any one layer or stratigraphic unit. A complete gradation between limestone and dolomite is uncommon.

The value and use of carbonate rocks are determined by their composition. High-calcium limestone and high-purity dolomite have a great variety of uses in the chemical and metallurgical industries and are by far the most valuable of these rocks. High-calcium limestone is defined here as consisting of at least 97 percent $CaCO_3$ by weight, but many writers use 95 percent as a defining limit (Ericksen and Cox, 1968, p. 227). High-purity dolomite has at least 87.5 percent $CaMg(CO_3)_2$ (40 percent $MgCO_3$). Pure dolomite, $CaMg(CO_3)_2$, consists of 45.7 percent $MgCO_3$ by weight. Cement limestone may contain a considerable amount of clastic impurities if they are relatively uniformly distributed throughout the rock and provides the alumina and silica needed for portland cement. Cement limestone must contain less than 6.5 percent dolomite because raw materials for portland cement cannot contain more than 3 percent $MgCO_3$; the specifications for portland cement permit no more than 5 percent MgO. During the manufacture of cement, CO_2 is lost from $CaMg(CO_3)_2$, causing relative enrichment of the magnesium in the finished product (Boynton, 1957, p. 98).

Carbonate rocks containing more than 25 percent fine clastic material are unsuitable for any use except as fill for construction. Chert in crushed stone to be used as concrete aggregate is undesirable because the chert may react with the cement, and the resulting chemical compounds might weaken the concrete and cause spalling.

PRODUCTION, USES, AND DESIRABLE PROPERTIES

The present consumption of limestone is immense; more than 628 million tons of limestone and dolomite was used in the United States in 1969 (fig. 43). Although essential to industry, limestone and dolomite are among the cheapest of the mineral commodities—the average price of crushed limestone and dolomite at domestic quarries was $1.46 per ton in 1969. Commonly, a user pays more for shipping the limestone than for the rock itself. For example, the M. W. Kellogg Co. (1972, p. 13) reported the following freight rates for crushed stone in the United States, expressed in cents per ton-mile: truck, 5–10 (at 10 miles) to 2–5 (at 100 miles); rail, 4.5–6 (at 10 miles) to 0.75–1.5 (at 250 miles); and water (barge or ship), 0.9–1.5 (at 20 miles) to 0.25–0.50 (at 500 miles). Because of shipping costs, limestone of relatively poor quality may be used in preference to better quality limestone that must be shipped in from a greater distance. For example, the Vanport Limestone is mined in western Pennsylvania, eastern Ohio, and northern West Virginia for use in nearby steel plants, even though it contains only 90–95 percent $CaCO_3$ instead of the 95 percent or more $CaCO_3$ usually required for flux.

Most limestone and dolomite is produced from open pits or quarries ranging from tens to a few hundreds of feet in depth. Relatively small amounts of stone, chiefly high-purity material, are produced from room-and-pillar underground mines, most of which are less than 500 feet deep. Open-pit mining

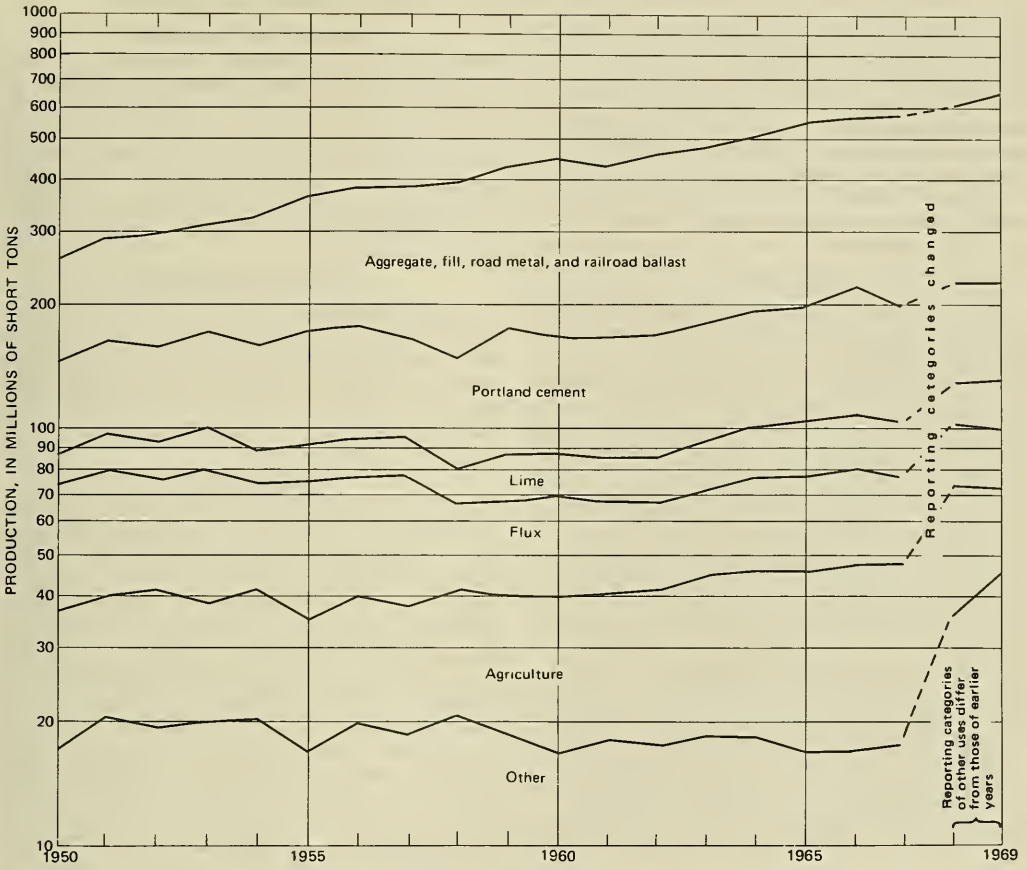

FIGURE 43.—Production and use of limestone and dolomite in the United States, 1950–69. Data from U.S. Bureau of Mines "Minerals Yearbook."

and crushing and screening of rock are noisy and dusty operations and, hence, are commonly curtailed or banned in populous areas.

CONSTRUCTION STONE

Nearly two-thirds of all limestone produced in the United States in 1969 was used in construction, chiefly as aggregate, fill, and road metal. The stone for these purposes must be clean, hard, strong, and free of soft or friable material; it should break into irregular but nearly equidimensional fragments; road metal should also be resistant to abrasion and have low porosity. Concrete aggregates should be low in reactive materials such as alkalis, soluble sulfides, and certain types of silica, particularly chert, that weaken concrete or even cause it to disintegrate. Many rocks are interchangeable with limestone for construction purposes.

PORTLAND CEMENT

Portland cement manufacture consumed about 15 percent of limestone production in the United States in 1969. Portland cement is a complex mixture of calcium silicate, calcium aluminate, and calcium aluminoferrite made by fusing a finely ground mixture of limestone and aluminous and siliceous ma-

terials, such as shale and silica sand (Ericksen and Thomson, 1968, p. 165). Suitable limestone contains as much as 25 percent clay and sand, generally not more than 6.5 percent dolomite, less than 0.5 percent phosphorous pentoxide, and only very small amounts of sulfur. In the Chicago, Pittsburgh, and Birmingham steel-producing areas, blast-furnace slag is used for making cement; on the Gulf Coast and in California, large deposits of sea shells are used as the source of $CaCO_3$. Cement made with slag and shells, however, accounts for only a small part of the total production.

FLUXES

Flux for blast and open-hearth furnaces consumed about 5 percent of carbonate rocks produced in the United States in 1969. During smelting, the magnesia (MgO) and lime (CaO) of these rocks combine with impurities, such as silica and alumina, to form a liquid slag that separates from the molten metal. About half the limestone used for flux comes from Michigan, and about 20 percent from Ohio, and 20 percent from Pennsylvania (U.S. Bur. Mines, 1953–1971, Minerals Yearbooks for 1950 to 1969). Limestone suitable for blast-furnace flux ranges from high-calcium limestone to calcareous dolomite containing as much as 31 percent $MgCO_3$ and not more than 5 percent silica, 2 percent Al_2O_3, and 0.05 percent sulfur (Dever and McGrain, 1969, table 22). It should contain at least 95 percent total carbonate; however, where the transportation cost of such stone is high, lower grade stone may be used. Limestone for open-hearth furnaces should contain at least 97 percent $CaCO_3$, less than 3 percent silica, less than 1.5 percent Al_2O_3, and low sulfur. Limestone suitable for fluxing nonferrous metals is similar to high-calcium limestone suitable for blast-furnace flux.

LIME

Lime manufacture consumed about 5 percent of the limestone produced in the United States in 1969. Lime is calcium oxide or calcium and magnesium oxide made by calcining (heating) limestone or dolomite to drive off the carbon dioxide. About one-third of the manufactured lime is used in metallurgy for smelting and for concentration or beneficiation of metalliferous ores, another third is used by the chemical industry, and the remainder is used in many ways, principally for water softening, pulp and paper manufacture, sugar manufacture, and sewage and waste treatment. Limestone suitable for high-calcium lime contains at least 97 percent $CaCO_3$. Low-magnesium lime contains 6–40 percent $MgCO_3$, whereas high-magnesium lime contains more than 40 percent $MgCO_3$; both types should have less than 3 percent noncarbonate impurities.

REFRACTORY DOLOMITE

Dead-burned or refractory dolomite, a fairly stable lime made by calcining dolomite at especially high temperature, used about one-half a percent of the carbonate rocks produced in 1969 in the United States. It is used chiefly for lining and patching of linings of open-hearth steel furnaces. Dolomite for this purpose should contain more than 37.5 percent $MgCO_3$ and at least 97 percent total carbonate minerals.

AGRICULTURAL LIMESTONE

Agricultural limestone consumed about 4 percent of the limestone produced in the United States in 1969. Agricultural limestone must have a calcium carbonate equivalent value of 80 or more. Pure limestone has a value of 100 and pure dolomite 108.6. (Dolomite has a larger value because magnesium is lighter than calcium.)

OTHER USES

About 8 percent of the limestone produced in the United States in 1969 had a wide variety of uses, each too small to be shown in figure 43. Among these are for alkali works, about 0.5 percent; glass manufacture, about 0.15 percent; and limestone sand, about 1.5 percent. Some other uses were not tabulated by the U.S. Bureau of Mines in 1969 but in past years have consumed comparable amounts of limestone. These include the manufacture of calcium carbide, beet sugar, pulp and paper, and industrial filler (whiting), and uses as pulverized limestone or dust that is applied to walls, roofs, and floors of coal mines to prevent or check coal-dust explosions, and as filter beds for water purification. The requirements for these uses vary, but, in general, limestone with a $CaCO_3$ content of at least 97 percent is required.

Limestone and dolomite probably will continue to be consumed in increasing quantities in the future and undoubtedly, new uses, particularly for high-purity stone, will become important.

GEOLOGIC ENVIRONMENTS

Limestone and dolomite form in a variety of environments, but they generally accumulate in warm shallow marine water. High-calcium limestone forms in those areas of free circulation with the open sea that are free of clastic sediments from nearby streams. Dolomite, however, is chiefly a rock of secondary origin, formed during diagenesis of limestone by partial replacement of $CaCO_3$ with $MgCO_3$ to form the mineral dolomite.

Most limestone is a lithified mixture of detrital grains and lime mud. The grains include whole and broken fossils, pellets of mud, and oolites composed of concentric layers of calcite precipitated around a nucleus. A complete gradation occurs between limestone composed entirely of grains and limestone composed entirely of limy mud. The mud is composed of chemically precipitated calcite and aragonite and tiny calcareous fragments from organisms. The carbonate sediments respond to marine currents as do land-derived noncarbonate sediments, and some limestone layers are finely laminated and show graded bedding or even crossbedding.

Reef limestone is formed in place as rigid frameworks build up by colonial organisms, such as corals, bryozoa, and algae. Organic reefs form only under ideal conditions of clear shallow marine water, warm temperatures, and abundant food supply. Large reefs can form only where the water depth slowly increases. Detrital materials, including fragments eroded from the reef by wave action and shells of noncolonial organisms, accumulate around the reef and commonly make up a much greater volume than the rigid reef rock.

Dolomite forms in some places where sea water evaporates and also forms indirectly as a partial replacement of calcite in limestone by magnesium from calcium-depleted brines of evaporated sea water percolating through limestone. Today, dolomite forms on broad, nearly level flats just above the level of high tide. These flats are intermittently flooded by sea water, during either spring tides or storms, and some of the water remains on the flats after the flooding. The water collects in small depressions where evaporation takes place, and various minerals may precipitate as the brine becomes more saline. Gypsum ($CaSO_4 \cdot 2H_2O$), the first mineral to precipitate, depletes the brine in calcium, causing a change in the ratio of magnesium to calcium from 5:1 in normal sea water to as much as 50:1. Dolomite forms by reaction of the magnesium-enriched brines with formerly deposited calcite and aragonite. Seasonal rainfalls may bring about a concentration or purification of the dolomite by dissolving impurities deposited by the brine; for example, gypsum, which is more soluble than dolomite, is thus preferentially dissolved and returned to the ocean. Dolomite also occurs in some evaporite sequences that were deposited in broad shallow seas of nearly stagnant or very slowly circulating water in an arid climate. In such shallow seas a salinity gradient developed, whereby the salinity increased as the distance from the open ocean increased.

DISTRIBUTION AND RESOURCES

Limestone and dolomite occur in most parts of the world and have formed throughout geologic time, but they are notably more abundant in rocks formed after shell-secreting organisms became abundant about 500 million years ago. Limestone and dolomite formations are widespread in the United States, and nearly every State has deposits adequate for construction and other uses that do not require chemically pure stone. High-calcium limestone and high-purity dolomite make up only a small fraction of all limestone and dolomite formations, and they occur in restricted areas. But even so, some high-purity carbonate formations are widespread, occurring in minable thicknesses nearly continuously over areas of many hundreds or even thousands of square miles. Although these nearly pure rocks are far less widely distributed than impure carbonate rocks, the resources are large and are sufficient to supply the growing needs of the Nation for hundreds or even thousands of years at anticipated rates of consumption.

The most extensive stratigraphic units of limestone and dolomite of the United States were deposited in the Paleozoic Era, when North America was extensively covered by shallow seas. Carbonate rocks make up a significant part of the thickness of the Paleozoic sedimentary sequence. Exploitable limestone and dolomite formations occur most extensively in the slightly deformed rocks of the midcontinent—especially in Kentucky, Tennessee, Missouri, and the States adjacent to the Great Lakes. Formations exposed in the folded and faulted parts of Appalachian and Rocky Mountains tend to be linear bands parallel to regional geologic structure and, thus, are more restricted in area. However, some parts of these mountainous areas, as in the Appalachian Plateaus and the plateau regions of the Western United States, are relatively undeformed and the nearly flat-lying units are at minable depths over wide areas.

Only a few formations will ultimately be the principal sources of high-calcium limestone and high-purity dolomite. The greatest quantities of high-calcium limestone occur in widely distributed formations of Mississippian age (table 69), whereas the greatest quantities of high-purity dolomite occur in formations of Ordovician and Silurian ages (table 70). Smaller deposits of high-quality limestone and dolomite occur in formations of other ages, and many formations that are chiefly impure rock locally contain minable deposits of high-purity limestone or dolomite. Some Ordovician formations

TABLE 69.—*Principal sources and some potential sources of high-calcium limestone in the United States*

Geologic age	Stratigraphic unit	Principal areas of occurrence of high-calcium limestone
Eastern and Central United States		
Tertiary	Ocala Limestone	Northwestern peninsula, Florida.
Pennsylvanian	Vanport Limestone (also a member of the Alleghany Formation).	Western Pennsylvania, northern West Virginia, eastern Ohio.
Mississippian	Greenbrier Limestone	Northern West Virginia, southwestern Virginia.
	Bangor Limestone	Northern Alabama, northern Georgia.
	Maxville Limestone	Eastern Ohio.
	Ste. Genevieve Limestone	Eastern Tennessee, northern Alabama, Kentucky, Indiana.
	Girkin Formation (formerly Gasper Formation).	Western Kentucky, northern Alabama.
	St. Louis Limestone	Missouri, Illinois.
	Salem Limestone	Southern Indiana.
	Warsaw Limestone	Southern Indiana, Kentucky, northern Alabama.
	Boone Formation	Northern Arkansas.
Devonian	Helderberg Group	New York.
	Jeffersonville Limestone	Kentucky, southern Indiana.
	Traverse Formation, as used by Shaver and others (1970), or Group.	Michigan, Indiana.
	Cedar Valley Limestone as used by Thiel and Schwartz (1941).	Southeastern Minnesota.
	Rogers City Formation	Northeastern Michigan.
	Dundee Formation	Do.
	Columbus Limestone	North-central Ohio.
Ordovician	Holston Limestone	Eastern Tennessee, southwestern Virginia.
	New Market Limestone	Southwestern Virginia.
	Newala Limestone	Northern Alabama.
	Valentine Member of Curtin Limestone of Kay (1943).	Central Pennsylvania.
	Annville Limestone	Southeastern Pennsylvania.
	Trenton Limestone	New York.
	Galena Dolomite and Platteville Limestone.	Minnesota, Illinois, Wisconsin.
Cambrian	Tomstown Formation	Panhandle of West Virginia.
Western United States		
Quaternary	Shell beds	Southern California coast and Texas coast.
Tertiary	Sierra Blanca Limestone	Southwestern California.
	Vaqueros Formation	Do.
	Martinez Formation	Do.
Cretaceous	Mural Limestone	Southeastern Arizona.
	Edwards Limestone	Central and western Texas.
Tertiary to Jurassic	Franciscan Formation and metamorphic rocks of nearly equivalent age (limestone occurs as lenticular bodies).	Coastal Range and California and southwestern Oregon.
Jurassic(?)	Limestone of Kings River area.	Southern Alaska.
Triassic	Limestone of Snake River area.	Southwestern Idaho.
Triassic and Permian	Isolated limestone deposits	Northeastern Oregon.
Permian	Ingleside Formation	North-central Colorado.
Permian to Mississippian	White Knob Limestone and Wells Formation.	Southeastern Idaho.
Carboniferous(?)	Oro Grande Formation	Central southern California.
Pennsylvanian or Mississippian.	Limestone lenses in metasediments.	Southwestern Oregon.
Mississippian	Madison Group	Western parts of Montana, Wyoming, and Colorado; southeastern Idaho, and northeastern Utah.
	Escabrosa Limestone	Southeastern Arizona.
	Redwall Limestone	Northern Arizona.
Devonian	Crystal Pass Limestone Member of the Sultan Limestone.	Southern Nevada.
Silurian	St. Clair Limestone	Central and eastern Oklahoma.
	Heceta Limestone	Southeastern Alaska.
Ordovician	Fernvale Limestone	Central and eastern Oklahoma.
Cambrian	Meagher Limestone	Western Montana.
Paleozoic (undifferentiated).	Limestone of Pico Blanco.	Southern coast of California.

TABLE 70.—*Principal sources and some potential sources of high-purity dolomite in the United States*

Geologic age	Stratigraphic unit	Principal areas of occurrence of high-purity dolomite
Eastern and Central United States		
Devonian	Geneva Dolomite	Southeastern Indiana.
Silurian	Niagara Group, Limestone, or Dolomite.	Wisconsin, Illinois, Michigan, Indiana, Ohio, Pennsylvania, New York.
Ordovician	Galena Dolomite	Northern Illinois.
Cambrian	Tomstown Formation	Western Maryland, western Virginia, and eastern panhandle of West Virginia.
	Shady Dolomite	Eastern Tennessee, southwestern Virginia.
	Ketona Dolomite	Northern Alabama.
Western United States		
Mississippian	Monte Cristo Dolomite or Limestone.	Southern Nevada.
Devonian	Water Canyon Formation	Northern Utah.
Silurian	Laketown Dolomite	Southeastern Idaho, northern Utah.
	Fusselman Dolomite	South-central and western New Mexico.
Ordovician	Bighorn Dolomite or Limestone.	Western Wyoming.
	Fish Haven Dolomite	Northern Utah.
Cambrian	Hasmark Formation or Dolomite.	Western Montana.
	Royer Dolomite	Southern Oklahoma.

contain deposits having exceptionally high calcite content—the Holston Limestone of eastern Tennessee, the Valentine Member of the Curtin Formation of central Pennsylvania (one of the purest limestones in the United States), and the New Market Limestone of western and southwestern Virginia. In the eastern panhandle of West Virginia, the Tomstown Formation contains units of high-calcium limestone and high-purity dolomite, both of which are intensively exploited. The chief source of high-purity dolomite in the United States is the Niagara Group (table 70) in western Ohio.

PROBLEMS FOR RESEARCH

Although the United States is self-sufficient in limestone and dolomite and reserves of these rocks are immense, the reserves of chemically pure limestone and dolomite are limited and decreasing because some deposits are being mined out, users continue to make more stringent specifications, land underlain by high-purity carbonate rocks is being preempted for other uses, and zoning regulations restrict or prevent quarry operations in populous areas. The cost of high-calcium limestone will increase as thick, near-surface layers close to the industrial centers are mined out. Future production increasingly will depend on selective mining of relatively thin layers of limestone, underground mining, and mining from deposits distant from industrial centers. High-calcium limestone resources are more endangered by urban spread than almost any other mineral resource, except perhaps for sand and gravel, and the need to identify and protect areas of high-calcium limestone for future use is pressing.

Future supply of high-purity dolomite in the United States is less of a problem than that of high-calcium limestone because far less high-purity dolomite is required by industry. Furthermore, immense resources of high-purity dolomite occur in the Great Lakes region, near eastern industrial centers where most dolomite is used. The extensive high-purity dolomite of the Niagara Group (table 70) is an example. Resources of high-purity dolomite in the United States should be adequate for thousands of years. Shipping costs will continue to be a major factor in the future sources of supply of high-purity limestone and dolomite, particularly in the Western United States. These costs will rise as more distant sources are exploited, which probably will bring about the use of less pure stone nearer the user.

Although much general information about potential resources and distribution of chemically pure limestone and dolomite in the United States is available, detailed information about the chemistry and the distribution of high-quality stone in most formations is relatively sparse. Systematic study of these formations should be undertaken to identify favorable areas that can be protected from urban spread and thus assure an adequate supply of inexpensive stone in the future.

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LITHIUM, CESIUM, AND RUBIDIUM— THE RARE ALKALI METALS

By James J. Norton

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ABSTRACT OF CONCLUSIONS

Lithium, cesium, and rubidium, though rare in comparison with sodium and potassium, are abundant relative to the apparent commercial need for them. Lithium and cesium both form independent minerals in pegmatites. Lithium production from brines has increased so greatly in recent years that it has taken much of the market away from pegmatitic lithium. Rubidium forms no known independent minerals but exists chiefly as a substitute for potassium, especially in minerals formed late in the crystallization of pegmatites. Most commercial rubidium and some cesium have been obtained as byproducts of processing lepidolite.

The world's proved and probable reserves of lithium, most of which are in the United States, are 1,200,000 tons, or about 400 times the 1970 consumption. Additional resources in known lithium regions are about 10 million tons, and even this large figure probably could be increased many times by intensive search throughout the world.

World cesium reserves are 100,000 tons, which also is vastly greater than consumption and probably much less than could be found if needed. For rubidium, meaningful resource estimates cannot be made, but surely the supply obtainable at current prices is plentiful.

To prepare for new uses frequently proposed, especially uses of lithium, knowledge of the geology of rocks and waters that are enriched in rare alkalis should be increased.

INTRODUCTION

The alkali metals include, in addition to the abundant elements sodium and potassium, four much rarer members—lithium, cesium, rubidium, and francium. Lithium, atomic number 3, has been mined and used since the latter part of the 19th century, and by the 1950's it had become the basis for an industry of moderate size. Cesium and rubidium, atomic numbers 55 and 37, respectively, have never been used in quantities of more than a few thousand pounds per year, virtually all of which is a byproduct from lithium mining. Cesium in the mineral pollucite does occur in deposits that would be minable for cesium alone if the market were larger, though even in these deposits cesium is a byproduct in the sense that it is generally found during exploration

or mining for lithium minerals. Rubidium is not known to form any minerals of its own and occurs only as a minor constituent in minerals of other kinds, especially potassium minerals, and thus appears destined to continue as a byproduct. Francium, atomic number 87, is virtually nonexistent and may be disregarded in any discussion of mineral resources.

The phrase "rare alkalis" is to some degree misleading. The known quantities of lithium and cesium, and probably also rubidium, obtainable under economic conditions resembling those of the present or the recent past are far greater than the amounts needed for current use or even for any but the most fanciful uses predicted for coming decades. New discoveries have often made supplies available to the market long before a demand for the supplies materialized. Publicity about these discoveries, which too frequently magnifies evidence that uses of these commodities will increase, tends to put the merit of even good deposits in question when after some years they have still not been mined, for the fact that the shortcoming lies not in the supply but in the demand may go unrecognized. The adequacy of lithium reserves to support new uses has been questioned even in recent years. Yet it was known two decades ago, and has been stated in the published record since at least 1955, that lithium reserves are enormous and that large additional reserves could almost certainly be discovered, as in fact they have been in the intervening years.

The geologic distribution of lithium, cesium, and rubidium is in many respects parallel to the distribution of the common alkali metals sodium and potassium, which is expectable from their chemical similarities. All the principal lithium minerals, as well as the cesium mineral pollucite, are obtained from granitic pegmatite, which is a generally coarse-grained rock consisting chiefly of sodic and potassic feldspars, quartz, and muscovite. Most of the rubidium and some cesium used commercially have been extracted from residues of the processing of lepidolite, a lithium-rich mica of pegmatite. Lithium from brines, which have long been a modest source, has in recent years come to dominate the market.

Crustal-abundance estimates in table 71 show rubidium as the most common of the rare alkalis, lithium as a distant second, and cesium as very meager. The abundance of rubidium may surprise those whose chief acquaintance with rare alkalis is through knowledge of industry patterns or awareness of the absence of deposits comparable to those of lithium and cesium. Rubidium seems to substitute so readily for potassium in minerals that it is never greatly concentrated in nature, whereas lithium and cesium are less able to proxy for other elements and thus must under some conditions form independent minerals. Granitic rocks are the predominant host of all the rare alkalis. During weathering and sedimentation, rubidium and lithium, and probably cesium as well, are for the most part dispersed in clays. All deposits that have been economic sources of rare alkalis formed either in the pegmatite phase of granitic activity or through the development of unusual varieties of brine.

TABLE 71.—*Crustal abundance, in parts per million, of rare alkali metals*

[Data from Heier and Billings (1970)]

	Rubidium	Lithium	Cesium
Upper continental crust	110	20	?
Lower continental crust	15	10	?
Continental crust	48	13	3
Oceanic crust	2.5	10	1
Crust	37	12	?

LITHIUM

Lithium is by far the most economically important of the rare alkalis, and for this reason it will be discussed first and at greatest length.

Most users of lithium products purchase lithium in the form of manufactured chemical compounds, of which the most common are the carbonate, hydroxide, bromide, chloride, hypochlorite, and stearate, and butyl lithium. Lithium metal and alloys are also produced. Lepidolite and petalite and lesser quantities of other lithium minerals go directly into some kinds of glass and ceramics. Additional uses of lithium products are in grease, in the manufacturing of air-conditioning systems and alkaline storage batteries, in fluxes for welding and brazing, and in metallurgy.

Two of the more frequently mentioned potential uses for lithium could someday cause a very great increase in demand. One is for anodes and as a constituent of the electrolyte in storage batteries to power electric automobiles. The other is as an energy source, to breed tritium for fusion reactions.

The United States is generally self sufficient in lithium and will remain so under any likely future circumstances. The only shortage is in lepidolite and petalite for glass and ceramics, and substitution may be practicable for some of these uses. Unfortunately, domestic production figures have not been published for many years, and few export figures are available; thus, it is impossible to calculate relationships among production, consumption, imports, and exports.

Lithium was obtained chiefly from pegmatites throughout most of the history of the industry,

though after 1938 a sizable supply came from brine at Searles Lake, Calif. In 1966, however, production started from brine at Silver Peak, Nev., and this deposit seems to have become the world's largest source of lithium. Certain clays are also known to be enriched in lithium, but no attempt has ever been made to mine them.

LITHIUM DEPOSITS IN PEGMATITES

GEOLOGY

Pegmatites containing lithium minerals can be divided into two categories: (1) deposits of spodumene in which there is so little change in the composition or texture of the rock from one place to another that it can be said to be virtually homogeneous; and (2) deposits of spodumene or other lithium minerals that are segregated into a series of zones of different composition or texture, in places accompanied by replacement bodies and fracture-filling units.

The Foote Mineral Co.'s deposit at Kings Mountain, N. C., stands out as the best example of a homogeneous lithium-rich pegmatite. Kesler (1961) showed that the mineral content, in weight percent, is: spodumene, 20 percent; quartz, 32 percent; albite, 27 percent; microcline, 14 percent; muscovite, 6 percent; and other minerals, 1 percent. Crystals of spodumene and microcline are as much as 3 feet long, but most are less than 1 foot long. The other minerals are all finer grained. The deposit consists of many irregularly shaped, interfingering bodies, some large and some small; yet, the only noticeable inhomogeneity is the absence of spodumene and microcline within a few inches of some contacts, where a narrow wall zone consists of quartz, albite, and muscovite.

Many spodumene-rich pegmatites have a more conspicuous wall zone of this same kind and are assigned to the zoned category, though actually they may differ only slightly from the homogeneous pegmatites. The Beecher No. 2 pegmatite in the Black Hills, S. Dak., has a well-defined wall zone barren of lithium minerals, but otherwise it resembles the homogeneous pegmatites at Kings Mountain in its composition and texture, and also in its structural irregularities. It is rightfully called a zoned pegmatite, but it can be regarded as being gradational between the homogeneous pegmatites and the complexly zoned pegmatites.

Some lithium pegmatites contain many zones, of which one or several may contain lithium minerals. The Bob Ingersoll No. 1 pegmatite in the Black Hills has been a major source of lepidolite from its innermost zone and contains amblygonite in another zone; yet it carries no lithium minerals in the four remaining zones. On the other hand, the nearby Etta pegmatite contains spodumene throughout the three largest zones; only the narrow wall zone and the small quartz core are barren.

MINERALOGY

Spodumene is by far the most abundant lithium mineral of pegmatites. Other important minerals are lepidolite and petalite. Additional minerals from which lithium has been obtained are amblygonite and eucryptite. Table 72 shows the chemical formulas and Li_2O contents of these minerals.

TABLE 72.—*Composition, in weight percent, of lithium minerals mined from pegmatites*

Mineral	Formula	Maximum theoretical content of Li_2O	Li_2O content of commercial concentrates
Spodumene	$LiAlSi_2O_6$	8.0	4 –7.5
Lepidolite	$KLi_2AlSi_4O_{10}F_2$[1]	7.7	3 –4.5
Petalite	$LiAlSi_4O_{10}$	4.9	3.6–4.7[2]
Amblygonite	$LiAlPO_4(F,OH)$	10.2	7.5–9.5
Eucryptite	$LiAlSiO_4$	11.9	5.5–6.5[2]

[1] Formula for polylithionite end member. Natural lepidolite has various proportions of muscovite molecule.
[2] For Bikita, Rhodesia (Cooper, D. G., 1954, p. 450)

Spodumene is invariably accompanied by quartz, and, except in the inner zones of a few zoned pegmatites, it is also accompanied by feldspar. Ordinarily spodumene constitutes between 20 and 25 percent of the rock mined, whether in a homogeneous pegmatite or in a zone of a zoned pegmatite. All deposits that have been successfully mined carry at least 1.0 percent Li_2O.

Lepidolite (lithium-rich mica) ranks as an important source of lithium mainly because of its abundance at Bikita, Rhodesia, but it also has been mined at several other localities. It occurs mainly in the central part of zoned pegmatites, where its chief associates are albite and quartz.

Petalite has been found in very few places, but where it does occur, it commonly is abundant. Virtually no petalite has been found in the United States. Descriptions of such foreign deposits as the one at Bikita, Rhodesia (Cooper, 1964), show that the petalite is mainly in intermediate zones of zoned pegmatites, where it is associated with quartz, feldspar, and spodumene. Eucryptite is common as an alteration product of spodumene at Bikita, though very rare elsewhere.

Amblygonite is widely distributed in pegmatites, but rarely if ever does it form as much as 10 percent of any sizable body of rock. It has been mined chiefly from very coarse grained parts of certain zoned pegmatites that yielded crystals large enough to be concentrated by hand. Its large lithium content made

it the favored source, and at times the dominant source, of lithium in early years of the industry, but in recent decades its share of the market has been small.

Other lithium-bearing minerals in pegmatites are zinnwaldite and allied micas, triphylite-lithiophilite and similar phosphates, and bikitaite. None of these have been commercially important sources of lithium, nor are any likely to become important in the future.

PETROGENESIS

CRYSTALLIZATION OF LITHIUM-RICH PEGMATITE

How lithium pegmatites crystallize has been greatly elucidated by the experimental work of Stewart (1960, 1963, and written communs.). The geochemical development of lithium pegmatites has the remarkable result that in deposits of spodumene, petalite, or lepidolite the grade is rarely much lower than 1.0 percent or much greater than 2.0 percent Li_2O. Stewart has found that the system albite-quartz-spodumene-water has a thermal minimum (analogous to the well-known granite minimum) at a composition characteristic of homogeneous spodumene pegmatites and of feldspar-quartz-spodumene zones of zoned pegmatites. The magma may at the outset precipitate only quartz and feldspar, forming the spodumene-free units observed in the outermost parts of many spodumene pegmatites, but when the lithium concentration of the melt reaches that of the thermal minimum, a lithium mineral will begin to be precipitated. Ordinarily the lithium mineral will be spodumene, which crystallizes from the melt at low temperatures and high pressures. Under lower pressure (P_{H_2O} less than about 2,000 bars) the liquidus does not reach the low temperature of spodumene crystallization, and the higher temperature mineral, petalite, must crystallize from the melt. Not uncommonly, as the solidified pegmatite becomes cooler, the petalite changes to spodumene plus quartz.

As crystallization from the melt proceeds, the composition must remain feldspathic and have an Li_2O content of no more than about 2 percent. Yet inner zones of some pegmatites are exceedingly quartzose, and a few inner units contain more than 2 percent Li_2O. Stewart discovered that the solids dissolved in the gas coexisting with the melt are highly siliceous. He thus attributes quartzose inner zones and also units of abnormally high lithium content to precipitation from the gas.

Hydrothermal investigations by Munoz (1971) show that lepidolite is stable only at low temperatures in pegmatitic mineral assemblages and that it can form by subsolidus reaction of spodumene and potassic feldspar in the presence of a fluorine-bearing aqueous gas. Textural and structural relations of some lepidolite to spodumene and microcline at many localities indicate that it does indeed form by replacement during cooling of pegmatite. Yet most lepidolite is in the innermost zone of the pegmatite, quite separate from any zone containing other lithium minerals. Though such lepidolite zones have a very disordered texture, with abundant veining and corrosion features, they lack evidence of preexisting lithium minerals. The core of the Bikita pegmatite has quartz as the principal associate of lepidolite and may have crystallized directly from the siliceous gas described by Stewart. In other pegmatites, however, feldspar is abundant in the lepidolite core, and its origin thus becomes implausible as a product either of the gas or of the silicate melt. Nevertheless, if lepidolite can form at low temperatures by subsolidus reactions as a replacement mineral in outer zones, then it should also be stable as a direct precipitate of whatever residual fluid remains at these temperatures trapped in the center of the pegmatite.

ORIGIN OF PEGMATITIC MAGMA

How a lithium-rich magma is generated can be stated in generalities but with few details. Localities containing pegmatites ordinarily also contain granite of approximately the same age that is universally regarded as the source of the pegmatitic fluid or in some other way closely related to it. The granites that accompany pegmatites, being of low calcium content and in some instances having virtually no calcium at all, are probably formed by melting of calcium-poor sediments rather than by fractionation of basic magmas. If so, then only where lithium is available in the zone of the melting—presumably from clays that have been carried to great depths—can lithium pegmatites result, which would account for the absence of lithium minerals in many pegmatite regions.

How granites, which rarely contain much more than 100 ppm (parts per million) lithium, can generate pegmatitic magma of generally granitic composition but with several thousand parts per million lithium is a formidable question. In the Georgia Lake area, Ontario (Pye, 1965, p. 52–54), and in the Black Hills of South Dakota, the granite near lithium pegmatites tends to be of higher lithium content than elsewhere. This might be viewed as implying that the granitic magma fractionated to produce a lithium-rich magma were it not that

pegmatites as a rule contain either a great amount of lithium or virtually none at all; very small areas can contain both kinds, with few or no pegmatites of intermediate lithium content. This bimodal distribution indicates that the process of forming a lithium-rich magma involves more than simple concentration of lithium in granitic magma. D. B. Stewart (oral communs.), who has pondered this problem at length, has suggested that minerals of the granite, some of which can carry many hundreds of parts per million lithium, returned their lithium to the residual melt during reactions at a late stage of magmatic crystallization. Whether a pocket of residual melt could be in contact with, or have access to, enough of the solidified granite to obtain the requisite amount of lithium, and why it should seldom if ever crystallize in place but instead be expelled to crystallize elsewhere, are questions that diminish the attractiveness of this ingenious proposal.

That the lithium-rich magma was derived from granite magma, by processes not now understood, remains likely, but it is by no means a certainty. An alternate possibility is that lithium-rich magma formed in the zone of anatexis, independently of the granite magma, from partial melting of metasediments enriched in lithium. This origin is particularly appealing for large pegmatites, such as those at Kings Mountain, N. C., which have the same composition as at the minimum melting temperature in the feldspar–quartz–spodumene system. If a body of magma thus formed retains its individuality during upward movement, it becomes a lithium-rich pegmatite; if it merges with nearby granite magma, the result is granite with a somewhat higher than normal lithium content.

LITHIUM PEGMATITE LOCALITIES

The known lithium deposits of the world are numerous and widely distributed, but only a few have been economically important. The outstanding deposits are at Kings Mountain, N. C.; Barraute, Quebec; and Bikita, Rhodesia; and in the Karibib and Warmbad districts of South West Africa. Many other localities are known to be promising. Production figures presented by Schreck (1961, tables 9–12) provide a means of gaging the amount of lithium mining during past years at places throughout the world.

UNITED STATES

The dominant lithium district in the United States is Kings Mountain, N. C., where an area about 25 miles long contains many spodumene-rich pegmatites. The largest of these deposits, owned and mined by the Foote Mineral Co., has been described in detail by Kesler (1961).

Other areas in the United States contain pegmatites that are rich in lithium but too small to compete with equally rich but much larger deposits in North Carolina. The foremost among these areas is the Black Hills of South Dakota, which was the main source of lithium in the United States before the 1950's. All the production of the Black Hills has been from relatively small well-zoned pegmatites. The chief lithium mineral is spodumene, but the output includes a moderate quantity of lepidolite and most of the amblygonite mined in the United States. Lepidolite has also been extracted at the Harding mine near Dixon, N. Mex.; at the Stewart mine in the Pala district, California; and at the Brown Derby mine in the Quartz Creek district, Colorado. Other lithium pegmatites, most of which contain spodumene as the lithium mineral, have been found in Arizona, Wyoming, Massachusetts, New Hampshire, and Maine.

CANADA

The Quebec Lithium Corp.'s spodumene mine at Barraute, near Val d'Or, Quebec, is the most important of the known deposits in Canada and is the only one with a record of large production. The several pegmatites in this mine are virtually unzoned and consist mainly of albite, quartz, and spodumene.

The Tanco pegmatite (named from the Tantalum Mining Corp. of Canada, Ltd.) at Bernic Lake, near Lac du Bonnet, southeast Manitoba, which was earlier known as the Chemalloy and still earlier as the Montgary pegmatite, has drawn widespread attention as a potentially important source of lithium. This is a well-zoned pegmatite in which spodumene is the predominant lithium mineral but in which lepidolite is also abundant (Hutchinson, 1959; Wright, 1963; Howe and Rowntree, 1966) and petalite is present (Černý and Ferguson, 1972).

For the many other lithium pegmatites that have been discovered in Canada, Mulligan (1965) is the most comprehensive source of information. The Val d'Or region, Quebec, and the region near Bernic Lake, Manitoba, have attracted the greatest interest and contain many of the deposits. Pegmatites at Georgia Lake (Pye, 1965) and at several other localities in western Ontario carry spodumene. An extensive area near Yellowknife, Northwest Territories, has long been known to have lithium pegmatites, some of which are well zoned (Mulligan, 1965, p. 85–87). Furthermore, in broad areas of the Cana-

dian Shield, largely covered by glacial drift, it seems unlikely that more than a modest fraction of the existing lithium pegmatites have been found.

SOUTH AMERICA

Pegmatites in northeastern Brazil have been mined for both spodumene and amblygonite. The production, though small, is enough to encourage hope that more can be found.

Argentina is the only other South American country that has been a source of lithium, but whether its pegmatites have a significant potential is questionable.

AFRICA

Lithium pegmatites have been found in so many parts of Africa that only the outstanding localities can be mentioned here. The Bikita pegmatite in Rhodesia is preeminent. Cooper (1964) and Martin (1964) described this as a well-zoned pegmatite, 5,400 feet long, that contains abundant lepidolite and petalite and lesser quantities of spodumene, amblygonite, and eucryptite. The only other localities with a notable record of production are the Karibib and Warmbad districts, South West Africa, which contain zoned pegmatites described by Cameron (1955) that have been sources of lepidolite, petalite, and amblygonite. The Manono tin deposits, Republic of the Congo (Zaïre), have attracted interest as potential sources of lithium. These deposits are in two pegmatites, each said to be 3.5 miles long and 150–2,500 feet wide and to contain 10–25 percent spodumene (Kesler, 1960, p. 527).

EURASIA

Lithium pegmatites are known in many parts of Europe and Asia, but none of the deposits have a record of large production nor is there published evidence for large reserves. The chief localities are in Czechoslovakia, France, East Germany, Portugal, Spain, Sweden, Soviet Union, India, and Korea. The best known of the western European deposits is the Varuträsk pegmatite in northern Sweden, which contains lepidolite, petalite, spodumene, and amblygonite (Quensel, 1952, p. 53–55). France and Portugal have each produced more than 4,000 tons of lepidolite (Schreck, 1961, table 9). In the U.S.S.R., deposits on Kola Peninsula and in the Altai Mountains may be important, but available published data are not adequate for evaluating them.

AUSTRALIA

Several pegmatite districts in Australia are known to have lithium minerals, and the very small production may not be an accurate measure of the potential. Western Australia contains most of the known occurrences. Spodumene, amblygonite, lepidolite, and petalite have all been reported (Noakes, 1946, p. 9–12).

LITHIUM IN BRINES

Lithium has been obtained since 1938 from subsurface brine at Searles Lake, Calif., and since 1966 from another dry lake at Silver Peak, Nev. The Silver Peak deposit has become a very large supplier of lithium, probably the world's largest, but production figures are unpublished.

At Searles Lake the lithium is from an operation in which potassium chloride and sodium carbonate, sulfate, and borate are the main products. The brine contains about 0.015 percent Li_2O (Ryan, 1951, table 1), or 70 ppm lithium, which is extracted as dilithium sodium phosphate that contains about 21 percent Li_2O.

At Silver Peak, according to Barrett and O'Neill (1970), the brine contains 300 ppm lithium and 10–15 percent other dissolved constituents, of which chlorine and sodium are by far the most abundant. Lithium is the sole product. The well field from which the brine is obtained extends over an area of about 2 square miles, but the entire playa covers about 32 square miles. Clays, silts, sands, and evaporites are saturated with brine to a depth of at least 600 feet and possibly to 1,500 feet. I. A. Kunasz, in a 1970 Pennsylvania University doctorate thesis, "Geology and Geochemistry of the Lithium Deposit in Clayton Valley, Esmeralda County, Nevada," showed that the playa sediments have abundant hectorite obtained by erosion from nearby tuff. The hectorite was probably formed originally by hydrothermal alteration along a fault. Lithium of the brine, according to Kunasz, was leached from the tuff, and additional lithium may have been contributed by hot springs at the periphery of the basin.

The development of the Silver Peak locality has, by putting substance into what previously was only a promise, greatly increased interest in lithium of brines. Earlier analyses of saline deposits either indicated no more than teasing amounts of lithium, which implied that nothing better than byproduct lithium, as at Searles Lake, would ever be found, or were themselves of dubious validity (Norton and Schlegel, 1955, p. 340). An additional source of production has now been developed at Great Salt Lake (Indus. Minerals, Dec. 1971, p. 37), which contains about 60 ppm lithium that is extracted together with magnesium. The Salton Sea geothermal brine

has been found to contain 210 ppm lithium in addition to a wide variety of other potentially valuable constituents (White, 1968, table 1). Observations by Helen L. Cannon (written commun., 1972) indicate concentrations of lithium in several closed basins in Nevada and California, especially those surrounded by volcanic rocks.

Foreign localities have as yet received little attention. Chong (1971, p. 26) has found that lithium is concentrated in subsurface potassic brine in the Salar de Atacama of northern Chile. Though analyses are unpublished, the average grade is reported to be 2,000 ppm lithium (Mining Jour., June 26, 1970, p. 597; Guillermo Chong, written commun., Aug. 21, 1972). This seems too high to be accepted without confirmation but is nonetheless an indication that lithium-rich brines exist in western South America as in western North America.

All these lithium-rich brines are associated with continental sediments. Analyses of marine evaporites are invariably discouraging.

OTHER LITHIUM DEPOSITS

Fragmentary evidence has been cited from time to time to show that there may be other deposits of potential commercial value (Norton and Schlegel, 1955, p. 332–333, 336–337, and 341). Hectorite (a magnesium-rich bentonite) at Hector, Calif. contains about 1 percent Li_2O (Ames and others, 1958, table 3). Other clay deposits, which contain 0.2–0.5 percent Li_2O, have been recorded near Amboy, Calif. (Foshag and Woodford, 1936, table 1, p. 241), Kirkland, Ariz. (Norton, 1965), and Spor Mountain, Utah (Shawe and others, 1964). Kesler (1960, p. 524) mentioned an average content of 0.5–1 percent Li_2O in the shaly matrix of borate deposits at Boron, Calif. During study of zeolitic tuffs in lake beds of the southwestern States, R. A. Sheppard (written commun., 1972) found that lithium not infrequently attains levels of several hundred parts per million in montmorillonoid clay minerals, especially in saline environments; a nearly pure separate of saponite from Pleistocene Lake Tecopa, Calif., has 0.34 percent Li_2O. Tardy, Krempp, and Trauth (1972) recorded the lithium contents of many additional clays.

Whether any metamorphic rocks or hydrothermal veins contain enough lithium to attract interest is unknown. The mineral ephesite, a sodium-rich margarite detected in emery deposits in Turkey and in manganese deposits in South Africa, contains as much as 3.85 percent Li_2O (Schaller and others, 1967, p. 1692), but so far as known, it is a rare mineral.

EXPLORATION AND MINING

Though sporadic production was recorded from a few localities in the 1880's and 1890's, the world's first lithium mining of consequence began in 1898 at the Etta mine, Keystone, S. Dak. For the next 40 years, the chief sources were small mines in which spodumene, amblygonite, and lepidolite were recovered by hand sorting. During this period, production of lithium minerals in the United States was generally less than 2,000 tons annually; but in five of these years it exceeded 4,000 tons, and in 1920, a record year, the production was 11,696 tons, valued at $173,002 (Schreck, 1961, table 10), which probably contained about 250 tons of lithium. During these early years, the Etta mine was the largest individual source of lithium, and the only other important sources were the Harding mine, Dixon, N. Mex.; the Stewart mine, Pala, Calif.; and the Tin Mountain mine, west of Custer, S. Dak. Domestic production during this period was far greater than production from other countries.

The first important change came in 1938, when the American Potash and Chemical Corp. began producing lithium at Searles Lake, Calif. This marked the beginning of a period in which large, fully mechanized operations took the place of small mines that depended on hand sorting.

Expanding use during World War II caused the production of lithium minerals to reach a new peak in 1944, when 13,319 tons was produced in the United States and 17,169 tons was produced in the entire world (Schreck, 1961, table 9). This large production was made possible by the introduction of mineral dressing techniques, especially by the Solvay Process Co. at Kings Mountain, N. C.

A sharp postwar slump, which lasted until 1950, was followed by the tremendous increase in production of the 1950's that soon far surpassed all previous records. The greatest incentive was the purchase of lithium hydroxide by the U.S. Atomic Energy Commission. By 1954, domestic output was 37,830 tons of lithium minerals, containing 1,142 tons of lithium; and world production was 102,763 tons (Schreck, 1961, tables 9 and 10). Domestic production figures have not been published since 1954. For other parts of the world, however, production in the latter years of the 1950's was record setting, reaching a maximum in 1957, when the total was about 170,000 tons of lithium minerals and concentrates (Schreck, 1961, tables 9 and 11), which probably contained about 3,500 tons of lithium. If, as seems likely, domestic production also increased after 1954, the world's maximum output, in 1957

or within a year or two thereafter, was probably between 5,000 and 6,000 tons of lithium.

Three mines furnished most of the world's lithium during this period. One was the spodumene mine at Kings Mountain, N. C. operated by the Foote Mineral Co., which processed its own ores. Another was the spodumene mine of the Quebec Lithium Corp. at Barraute, Quebec; its concentrates were processed by the Lithium Corp. of America at Bessemer City, N. C. The third was the mine of Bikita Minerals (Pvt.), Ltd., at Bikita, Rhodesia; lepidolite concentrates from this mine were processed by American Lithium Chemicals, Inc., at San Antonio, Tex.

The rate of production dropped greatly in 1960, when the last of Atomic Energy Commission contracts expired, but it was still large by the standards of the years prior to 1953. The principal raw material sources continued for several years to be the same as in the 1950's, but the processing and marketing patterns changed.

Another milestone came in 1966 when production began from Silver Peak and an accompanying price reduction not only encouraged increased consumption but also led the Quebec Lithium Corp. to withdraw from the market. Luckenbach (1972, p. 115) estimated that domestic consumption, expressed as $LiCO_3$, increased from 14,490,000 pounds (1,360 tons Li) in 1966 to 20,000,000 pounds (1,880 tons Li) in 1970. Corresponding figures for the world were 20,790,000 pounds (1,950 tons Li) in 1966 and 32,500,000 pounds (3,050 tons Li) in 1970. Although consumption diminished in 1971, the trend indicates that the industry will in a few years pass the record set in the 1950's.

RESERVES AND RESOURCES

Reserves of lithium have long been known to be enormous relative to annual consumption, and with the opening of the Silver Peak deposit the reported reserve figures have become astronomic. Most of the known supply and most of the consumption of lithium are in the United States. There is little reason to believe that the large size of reserves in the United States means anything except that the search for lithium has been most intense near home; the rest of the world may be as well endowed with lithium as the United States. It may seem surprising that efforts have been expended to find much more lithium than is likely to be used for many decades. The explanation is not that efforts have been wasted but that many lithium deposits are disproportionately large relative to their market and have resources that can be readily estimated from the data acquired during exploration and development of even a small mine.

Table 73 shows total world resource figures in three categories: (1) proved and probable reserves, (2) possible reserves and conditional resources, and (3) hypothetical resources. All the proved and probable reserves are backed by persuasive evidence that they exist and that they can be mined profitably under conditions prevailing now or in the recent past. Possible reserves are included with conditional resources because there is doubt about how to categorize many deposits. Many unexplored spodumene deposits, for example, have a grade equal to that at existing mines, and thus would ordinarily be regarded as having possible reserves; but because it is questionable whether a new spodumene mine could now be developed and operated profitably in competition with brines, these resources perhaps should be downgraded to conditional.

TABLE 73.—*Lithium resources, in short tons*

Locality	Identified resources [1]		Hypothetical resources [4]
	Proved and probable reserves [2]	Possible reserves and conditional resources [3]	
Kings Mountain, N. C	486,000	([5])	1,000,000
Black Hills, S. Dak	------	10,000	
Other pegmatite districts of the United States	------	1,000	
Silver Peak, Nev., brine	500,000	2,000,000	2,500,000
Salton Sea, Calif., geothermal brine	------	1,100,000	
Searles Lake, Calif	10,000	30,000	
United States, total (rounded)	1,000,000	3,100,000	3,500,000
Barraute, Quebec	84,000	------	
Bernic Lake, Manitoba	45,000	------	
Other resources in Canada	------	200,000	1,000,000
Canada, total	129,000	200,000	1,000,000
Bikita, Rhodesia	90,000	------	
South West Africa	4,000	------	
Other resources in Africa	------	------	1,000,000
Africa, total	94,000	------	1,000,000
South America brines	------	([1])	1,000,000
World total (rounded)	1,200,000	3,300,000	6,500,000

[1] Specific, identified mineral deposits that may or may not be evaluated as to extent and grade, and whose contained minerals may or may not be profitably recoverable with existing technology and economic conditions.
[2] Identified deposits from which minerals can be extracted profitably with existing technology and under present economic conditions.
[3] Specific, identified mineral deposits whose contained minerals are not profitably recoverable with existing technology and economic conditions.
[4] Undiscovered mineral deposits, whether of recoverable or subeconomic grade, that are geologically predictable as existing in known districts.
[5] Included in hypothetical resources.

RESOURCES IN PEGMATITES

UNITED STATES

Virtually all the domestic reserves of pegmatitic lithium, and a very large part of the world's reserves, are at Kings Mountain, N. C.

Kesler (1960, p. 525, and 1961, table 3) reported that measured (equivalent to proved) reserves in the main part of the Foote Mineral Co.'s deposit on June 30, 1959, were 20,746,297 tons of ore carrying 1.53 percent Li_2O, which amounts to 147,000 tons of lithium. Additional reserves, but in the indicated

(probable) category, were reported at the same time as 15,769,075 tons, presumably of the same grade (Kesler, 1960, p. 525), which adds 112,000 tons of lithium to the total. Elsewhere in the Kings Mountain district, the Lithium Corp. of America holds reserves that were reported as of May 20, 1963 (Clarke, F. F., written commun., 1963), to amount to 37 million tons at 1.32 percent Li_2O, or 227,000 tons of lithium.

Kesler (1960, p. 525) reported that the total reserves of the Kings Mountain district probably exceed all published estimates. The largest of the estimates is equivalent to 600,000 tons of lithium (Norton and Schlegel, 1955, table 5). These reserves were almost entirely in the inferred (possible) category, yet they are not much greater than the proved and probable reserves of 486,000 tons that have since been demonstrated. Certainly enough lithium to make up the difference is in the many small spodumene pegmatites of the region and in unexplored parts of the known large deposits. It is not unreasonable to suppose also that the district has additional large bodies of spodumene pegmatite, perhaps at great depth, perhaps even near the surface. The total of possible reserves, conditional resources, and hypothetical resources may well be placed at twice the known reserves, or about 1 million tons of lithium.

Of the many localities elsewhere in the United States that contain lithium pegmatites, only the Black Hills, S. Dak., is known to have a significant quantity of lithium minerals, and the estimate there is only about 10,000 tons of lithium (Norton, 1964, p. 130). Because lithium mining has been dormant in the Black Hills for many years owing to the area's inability to compete with mines elsewhere, its lithium should be classified as a conditional resource. An estimate of hypothetical resources for the Black Hills or other localities in the United States would be trivial in comparison with the estimate for Kings Mountain.

CANADA

The best known deposits in Canada are at the Quebec Lithium mine, Barraute, Quebec, and the Tanco deposit, Bernic Lake, Manitoba. The Quebec Lithium reserves are 15 million tons containing 1.2 percent Li_2O, or 84,000 tons of lithium, according to the account by Mulligan (1965, p. 46), who apparently preferred these figures to somewhat larger figures published elsewhere. At the Tanco deposit, Howe and Rowntree (1966, p. 210) placed lepidolite reserves at 107,700 tons with 2.24 percent Li_2O and spodumene reserves at 4,727,263 tons with 2.01 percent Li_2O, excluding ore that would have to be left as a pillar unless the lake were drained. These figures indicate a total of 45,000 tons of lithium in the Tanco mine.

Reserve estimates have been published for many other deposits in Canada. None of them have been mined, nor do any seem as attractive as the Quebec Lithium or the Tanco deposits, one of which was closed in the face of competition from Silver Peak and the other after many years of effort has yet to produce lithium. In these circumstances, the other Canadian deposits seem most suitably classified as conditional resources. Pye (1965, p. 26) has tabulated data from the Georgia Lake area, Ontario, that indicate a total of 62,000 tons of lithium. For other areas in Canada, Mulligan (1965, table 6) compiled estimates that amount to 84,000 tons of lithium. Quite surely there is additional lithium at Barraute, Quebec, where only the ore within 600 feet of the main shaft to a depth of 850 feet is included in the Quebec Lithium reserves nor should the ore excluded as a pillar at the Tanco deposit, which has 22,000 tons of lithium, be left wholly out of account. For the Yellowknife region, Mulligan (1965, p. 89) preferred to quote none of the existing reserve estimates but instead remarked that there is a "reserve of many millions of tons of material comparable to that developed elsewhere." Taken altogether, the existing information points to conditional resources of at least 200,000 tons of lithium in Canada.

The vigorous prospecting for lithium in Canada during the 1950's resulted in the recognition of a great number of deposits. Mulligan (1965, table 6) listed 67 known deposits and lithium localities. Yet, in the absence of successful lithium mining, except at Barraute, Quebec, enthusiasm quickly waned. It may be surmised that exploration thus far has discovered only a fraction of the total amount of lithium actually available. An estimate of hypothetical resources amounting to 1 million tons of lithium seems plausible.

AFRICA

The two principal sources in Africa have been the Bikita pegmatite, Rhodesia, and the Karibib and Warmbad districts, South West Africa. Symons (1961, p. 145–148) reported that on December 31, 1960, the reserves (here converted to short tons) at Bikita were 6,700,000 tons of various categories of material containing an average of 2.90 percent Li_2O, or 90,000 tons of lithium. For South West Africa, Kesler (1960, p. 527) estimated "about 350,000 tons of crude lepidolite ores mostly containing 20 to 50

percent recoverable lepidolite, and about 200,000 tons of crude petalite ores of somewhat higher yield." These figures suggest a total of about 4,000 tons of lithium.

No published data appear to be available to calculate resources in the Manono deposits, Republic of the Congo, though the quantity seems to be immense (Kesler, 1960, p. 527). Eilertsen (1965, p. 534) mentioned deposits in the Republic of Mali that have 8,000 tons of lithium. In several other African countries lithium minerals have been mined or the existence of lithium pegmatites has been noted. The hypothetical resources of Africa may be estimated at 1 million tons of lithium.

EURASIA, AUSTRALIA, AND SOUTH AMERICA

Noakes (1946) recorded resources amounting to 1,000 tons of lithium in western Australia, and Eilertsen (1965, p. 534) mentioned 4,000 tons in the same region. Lithium pegmatites in South America and Eurasia, though numerous and widespread, seem not to be large, or at least no published statement to the contrary has been noticed. The U.S.S.R. has at least a few deposits and has recently exported lithium compounds (Luckenbach, 1970, p. 83), though not in sufficient abundance to suggest that the country has any truly large mine.

The identified resources throughout the vast regions of Eurasia, South America, and Australia seem too small to take into account in this report, and there are no grounds at all for estimating hypothetical resources. This is not to say, however, that sizable resources will not ultimately be discovered.

RESOURCES IN BRINES

The key to any estimate of the overall lithium resources in brines is the Silver Peak deposit, Nevada, for which the Foote Mineral Co. reported reserves of 5–10 billion pounds of lithium (Foote Mineral Co., 1967, p. 24; Luckenbach, 1968). Details of how these reserve figures were computed have not been published, but enough numerical data are available so that with only a few assumptions the calculations can be approximately duplicated. Barrett and O'Neill (1970, p. 47) provided figures of 32 square miles for the area of the playa, 600 feet for the minimum thickness of the brine-bearing body, and 300 ppm for the content of lithium in the brine. Using these data and guessing that the brine occupies 40 percent of the volume and has a density of 1.1, one finds after making the appropriate calculations that the quantity of lithium approaches 5 billion pounds. It thus appears that the Foote 5–10 billion estimate applies to the entire 32-square-mile basin, and that the lower figure is to the known depth of brine in existing wells and the higher figure is to the probable average depth of the bottom of the basin. The grade apparently was assumed to be constant throughout the basin, and no estimate was made of how far the lithium content can be depleted before the grade becomes too low for profitable operation. The quantity, if any, of lithium that is being added to the brine from lithium-bearing clay and nearby hot springs, which would enlarge the reserves, seems to be regarded as too small to take into account.

With this background, it is possible to place the reserves and resources in categories. Probably 500,000 tons of lithium (20 percent of 5 billion pounds) in and near existing wells over a thickness of 600 feet can be called proved and probable reserves. Another 2 million tons of lithium at the same depth extending outward to the borders of the basin can be called possible reserves or conditional resources. The remaining 2,500,000 tons (or 5 billion pounds) of lithium seems best categorized as hypothetical resources.

For Searles Lake, Calif., published data have been used to make one estimate of 75,000 tons of Li_2O (Kesler, 1960, p. 524) and another of 90,000 tons of Li_2O (Norton and Schlegel, 1955, p. 346–347), or about 40,000 tons of lithium. Because lithium is only one of many products from Searles Lake, the question of how much of it will be extracted depends on the outlook for the rest of the operation. Production is about 100 tons of lithium annually (Smith and Irwin, 1966, p. 234). If, at the present rate of operation, the deposit has a life of 100 years, which seems as good an estimate as any that can be made from the host of figures available, then the ultimate output of lithium will be 10,000 tons. This amount can be labeled reserves, and the remaining 30,000 tons known in the deposit can be called conditional resources.

The few other lithium brines that have been identified have yielded very large resource estimates. Conditional resources of 1,100,000 tons of lithium are in the Salton Sea geothermal brine, which contains several other constituents of potential economic value (White, 1968, p. 313). The Salar de Atacama, Chile, is said to have 1,200,000 tons of lithium (Mining Jour., June 26, 1970, p. 597). Guillermo Chong (written commun., Aug. 21, 1972) confirms this estimate but says that an exploration program is now starting. Until this exploration is completed and the extraordinarily high supposed content of 2,000 ppm lithium is substantiated, the

potential of this deposit seems best combined with that of other lithium brines that may exist in South America to make an estimate of 1 million tons of hypothetical resources.

Great Salt Lake and probably other saline lakes in the world contain enormous quantities of lithium. Such lakes are omitted from table 73 because, unlike the other deposits included in the table, they are far more important for other purposes than as mineral deposits, and the likelihood is small that their lithium, which is at a very low grade, will be extracted in large quantity for a long time, if ever.

SUMMARY OF LITHIUM RESERVES AND RESOURCES

Table 73 shows that the world has proved and probable reserves of 1,200,000 tons of lithium plus nearly 10 million tons of possible reserves, conditional resources, and hypothetical resources. The proved and probable reserves alone would last the world 400 years at the 1970 rate of consumption.

Most of the vast quantities of lithium itemized in table 73 are in the United States, which suggests that much larger resources exist but remain undetected in foreign countries. By multiplying domestic resources by 16.0, which is approximately the ratio of the world's land area to that of the United States, one finds that world totals can probaby be brought to a level of 120 million tons of lithium. If domestic resources are in fact greater than shown in table 73, which is likely, and if the rest of the world does have proportionately as much lithium as the United States, which is also likely, then the actual world total is even larger. Any new discoveries are most likely to be made in localities with pegmatitic rocks in Canada, South America, Africa, and Australia, and in brines of western North and South America or geologically similar regions elsewhere.

Lithium-resource estimates by this author have sometimes been called conservative. They are in fact neither conservative nor liberal, but are merely the largest that can be projected from existing data. The real meaning of table 73 is that resources of lithium, in deposits comparable to those that have been mined, are virtually unlimited relative to any likely demand. If a truly large demand for lithium ever arises—for example, for batteries for electric automobiles or for nuclear-power generation, which, however inevitable their development may be, will not necessarily use much lithium—then the search for high-quality lithium deposits will be renewed, and resource figures will skyrocket even further. Prudence would, of course, require that deposits be identified and their reserves determined before any such large use actually begins.

CESIUM

Cesium, though of low abundance in the earth's crust, has large reservoirs relative to its exceedingly small consumption. Most of the production and nearly all the known reserves are attributable to the Bikita pegmatite in Rhodesia, a few pegmatites in South West Africa, and the Tanco pegmatite, Manitoba.

Uses that have most commonly been mentioned are in research and development of ionic engines for space travel and thermionic power generation, which thus far at least has also been associated chiefly with space flights. Otherwise the use of cesium is in infrared lamps, photomultiplier tubes, scintillation crystals, pharmaceuticals, and certain chemical processes (Heindl, 1970, p. 530).

GEOLOGY

Cesium is most abundant in zoned pegmatites, a few of which contain astonishingly large and rich deposits. It is also concentrated in natural brines during crystallization of salts from sea water, but reaches a maximum of only 20 ppm in the last precipitates, sylvite and carnallite (Michael Fleischer, written commun., 1972). Two analyses of the Salton Sea geothermal brine show 14 and 20 ppm cesium (White, 1968, table 1). If any brines are known to have greater concentrations of cesium, the facts seem not to have been published.

In pegmatites the most abundant (and for practical purposes, the only) cesium mineral is pollucite, $(Cs,Na)AlSi_2O_6$, which in commercial concentrates generally contains somewhat more than 20 percent Cs_2O. Analyzed pure pollucite from the Tanco pegmatite, which has the largest reserves, contains 36.2 percent Cs_2O (Nickel, 1961, p. 6). Handsorted material, because it is contaminated by quartz which resembles pollucite, has about 28 percent Cs_2O in the Tanco deposit (Hutchinson, 1959, p. 1534) and about 25 percent at Bikita (Cooper, 1964, p. 451). Other cesium-rich minerals include uncommon forms of beryl (as much as 9.5 percent Cs_2O), cesium kupletskite, avogadrite, and the rare borate rhodizite (Michael Fleischer, written commun., 1972).

Pollucite deposits have a conspicuous association with lithium pegmatites that contain lepidolite and petalite. The Bikita and Tanco pegmatites have the world's two largest lepidolite deposits and also the two largest pollucite deposits. Similarly in South West Africa, though the published record is not so clearcut on the subject, the pegmatites with lepidolite and petalite seem also to be the source of pollucite. In both the Bikita and the Tanco pegmatites, most of the pollucite is in a single large and

very rich lenticular unit on the hanging-wall side of the pegmatite, generally well removed from the lepidolite core and surrounded by a spodumene-rich intermediate zone containing petalite (Cooper, 1964, p. 450–451 and figs. 3, 6, and 7; Martin, 1964, p. 124 and pl. 8; Hutchinson, 1959, p. 1534 and figs. 2 and 5; Wright, 1963, p. 936 and pl. 1; Crouse and Černý, 1972, figs. 3 and 4).

PRODUCTION

Production and consumption figures for cesium are rarely published. Howe and Rowntree (1966, p. 211) say that the United States in 1964 used about 8 short tons of cesium salts and somewhat more than 3,000 pounds of cesium metal. In 1970, the United States imported 5,129 pounds of cesium compounds plus an unstated quantity of pollucite, and the U.S.S.R. imported 200 tons of pollucite containing about 40 tons of cesium (Kurtz, 1972). From these figures, the world's consumption now and in the immediate future may be gaged at only a few tons of cesium annually. Prices are high; the 5,129 pounds of cesium products imported in 1970 were valued at $189,056 (Kurtz, 1972), or about $37 per pound.

The principal source has been the Bikita pegmatite, mainly from pollucite but also as a byproduct of the extraction of lithium from lepidolite, which resulted in an alkali carbonate residue containing about 2 percent cesium. South West Africa has been the other source in recent years, and Mozambique has also yielded cesium (Howe and Rowntree, 1966, p. 211). Only about 100 tons of pollucite has been mined in the United States, mostly from the Tin Mountain pegmatite, Black Hills, S. Dak., but also from Oxford County, Maine. All these sources are likely to be dwarfed by the Tanco deposit during any expansion of the cesium market unless a now unanticipated source of cesium (for example, as a byproduct of brine processing) makes an appearance.

RESERVES AND RESOURCES

Reserves of the Tanco deposit have most recently been placed at 293,863 tons of pollucite with 23.67 percent Cs_2O, or 66,000 tons of cesium (Mining Engineering, April 1962, p. 18). At Bikita the dimensions of the pollucite body, as furnished by Martin (1964, p. 124 and pl. 8), imply about 25,000 tons of cesium. Reserves in South West Africa may also be sizable, but elsewhere in the world the known amount of pollucite is negligible. Nevertheless, the world's total reserves may be placed at very close to 100,000 tons of cesium, which is virtually infinite relative to the trivial annual consumption or to anticipated demand.

Estimates of conditional or hypothetical resources are not worthwhile in the absence of data and in the absence of any predictable need for a larger quantity of cesium. If one makes the plausible assumption that the ratio between cesium reserves and proved and probable reserves of lithium in pegmatites (about 1:7) will remain approximately the same as additional lithium deposits are developed, the world has resources of several hundred thousand tons of cesium.

RUBIDIUM

Rubidium resources cannot be appraised in the same way as lithium or cesium resources because no rubidium minerals or rubidium-rich waters have been found or seem likely to be found, and all rubidium recovered is byproduct. The amount of rubidium available suffices for the small demand, and probably other byproduct sources could be tapped to increase the supply without much effect on prices.

Consumption figures for rubidium are unpublished but apparently are even smaller than for cesium, which in some uses serves the same purpose as rubidium. Consumption is mainly in research and development, but rubidium is also used in vacuum tubes, photocells, and medicine (Heindl, 1970, p. 700–702). The main source in recent years has been the alkali carbonate residue of the lepidolite plant formerly at San Antonio, Tex., the stock of which has not yet been exhausted, but it is also a byproduct of the processing of pollucite (Heindl, 1970, p. 700).

The apparent absence of independent rubidium minerals is attributable to chemical properties which enable rubidium to substitute for potassium, a ubiquitous constituent not only of granites and clays, which have the highest average contents of rubidium (Heier and Billings, 1970), but also of pegmatites and evaporites, which are commonly enriched in rubidium. According to Michael Fleischer (written commun., 1972) the rubidium content of pegmatite minerals is as much as 3.0 percent in microcline, 2.1 percent in muscovite, 4.1 percent in biotite, 4.5 percent in lepidolite, and 0.85 percent in pollucite; minerals of the Tanco pegmatite reach or exceed these maximums (Nickel, 1961, tables 1 and 4; Petr Černý, written commun., 1972). Among evaporite minerals, the rubidium content is at most about 0.2 percent in sylvite and carnallite (Michael Fleischer, written commun., 1972). Because both sylvite and carnallite are formed in the last stages of crystalli-

zation of oceanic salts, it is clear that rubidium increases in concentration in the brine until very nearly the end. The same applies as granite progresses to pegmatite, and the increase doubtless continues to the late stages of crystallization of at least some pegmatites, especially those containing lepidolite and pollucite.

Exhaustion of the stock of alkali carbonate remaining from lepidolite processing at San Antonio will necessitate finding another source of rubidium. This is not likely to be difficult if the demand continues small and the price high. Development of any new large-magnitude use, beyond what can be supplied from byproduct sources, will require search for new deposits, which in all likelihood can be found somewhere among the wide range of natural substances containing concentrations of alkalis. A discovery of rubidium-rich pegmatites in Manitoba (Jambor and Potter, 1967) indicates that grades of at least 1.0 percent Rb_2O are possible. The large body of analytical data acquired throughout the world in making rubidium-strontium age determinations probably would provide useful leads to where rubidium deposits might be found. At present, however, data pointing to potential rubidium deposits, as well as data about future demand for rubidium, and in what chemical form it might be used, are so sparse that it is fruitless to attempt to estimate resources.

RESEARCH SUGGESTED

Because supplies of lithium, cesium, and probably rubidium are large relative to their market, there is no urgent need to find new resources. New uses for these elements are seriously considered from time to time, and some of these uses could ultimately create a large demand. To prepare for this eventuality, it would be prudent to learn more about which rocks and waters have concentrations of these elements and to identify the processes that cause these concentrations, so that search for new deposits can, at any future time, be intelligently planned. Geochemical investigations to date have been directed mainly at rocks, minerals, and waters that contain only slight amounts of these elements rather than at those likely to become economically productive, but they provide a basis for studies that can clarify how deposits form and where they might be found.

A desirable objective of future research is to facilitate the discovery of higher grade lithium deposits than those now known, so as to diminish cost of production—or, on the other hand, to show that no such deposits are likely to be found and all plans must be based on present costs. Lithium is unusual among mineral commodities in that the known resources in deposits of modest but minable grade are enormous, yet resources in truly high-grade deposits have never been found. This suggests that sizable high-grade deposits do in fact exist but have been overlooked.

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MAGNESIAN REFRACTORIES

By Alfred J. Bodenlos and T. P. Thayer

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ABSTRACT OF CONCLUSIONS

Magnesium-bearing compounds are processed into high-temperature refractories, indispensable as linings in modern steel furnaces; chemicals; and magnesium, the lightest of structural metals. They are derived from minerals, brines, and sea water.

Resources from which magnesium-bearing compounds may be recovered range in size from large to practically unlimited and are globally widespread. Identified resources of magnesite throughout the world total 12 billion tons, and those of brucite several million tons. Resources of dolomite, forsterite, and the magnesium-bearing evaporite minerals are enormous; magnesium-bearing brines must constitute a resource of billions of tons; and the resource contained in sea water is practically unlimited. The magnesium industry is highly competitive, and more costly sources, such as evaporite minerals, are little used. The bulk of magnesium-bearing compounds and the metal are recovered in the United States from sea water, brines, and dolomite, and elsewhere in the world from magnesite.

Magnesite deposits still are being sought, particularly those low in lime content. Opportunity for discovering such deposits in the United States is judged to be small, but is somewhat better in other parts of the world.

INTRODUCTION

Magnesium compounds are used to prepare refractories and chemicals; high-temperature refractories are indispensable as linings in modern steel furnaces and in certain parts of base-metal smelters, and reactive magnesium chemicals have many well-established industrial and pharmaceutical uses. Magnesium is the lightest of the structural metals and is used either as the pure metal or as an alloy wherever weight is a critical factor; magnesium competes with aluminum for these purposes to the extent that its higher price will allow. Magnesium metal also is used as a reductant in the extraction of titanium and certain other metals and as an oxygen scavenger; it is an important military incendiary material (Comstock, 1963; and Paone, 1970).

Magnesium-bearing raw materials are abundant, geographically widespread, and strongly competitive in world markets; they consist of minerals and brines of various geological origins (Davis, 1957; Birch and Wicken, 1951; and Wicken, 1960). This chapter, however, deals principally with the resources of magnesite, brucite, and olivine. Resources of dolomite, evaporites, and brines are described in other chapters of this volume.

Uses of the principal raw materials are shown in figure 44.

Magnesite and brucite, when calcined at low temperature (1,600°F) yield reactive or caustic-calcined magnesia that is used to make chemicals and cements. Magnesite and dolomite when calcined at high temperatures (3,000°F–4,000°F) yield inert

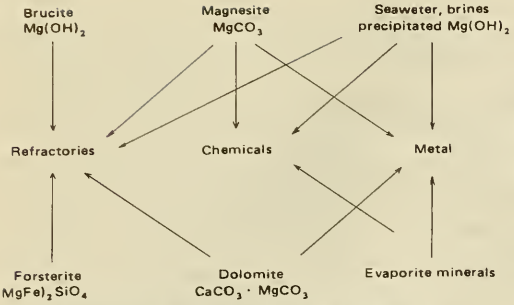

FIGURE 44.—Use of the principal raw materials of magnesium.

oxides (dead-burned magnesite, periclase, and dead-burned dolomite) used to make refractories. Sea water and magnesium-rich brines are treated with lime or caustic-calcined dolomite to precipitate magnesium hydroxide, which can be converted either to chemicals or refractories or to magnesium chloride, from which the metal can be extracted in electrolytic cells. When heated with ferrosilicon, caustic-calcined dolomite yields magnesium metal. Byproduct magnesium bitterns resulting from treatment of evaporite minerals are used to prepare magnesium oxide and have been used in the past in electrolytic cells to recover the metal. Forsterite molded into brick is fired at 3,000°F to produce a refractory that is inert to certain flue dusts and gasses, and when ground, the mineral forms a superior foundry molding sand.

The United States is virtually self-sufficient in magnesium-bearing raw materials, although its resources of low-cost low-lime magnesite are small; the country is a net exporter of magnesium metal and a net importer of magnesium compounds.

EXPLOITATION

Mining of magnesite deposits began in California in 1886, in Washington in 1916, and in Nevada in 1937; it ended in California in 1950 and in Washington in 1968. The large-scale use of calcined dolomite as a refractory began during World War I, and mining of brucite in Nevada began in 1934. Recovery of magnesium metal from deep-well Michigan brines began in 1916; sea-water recovery of magnesium oxide for metal production began in 1940, and in subsequent years sea-water magnesia supplanted magnesite as the prime source of refractory raw material. Magnesium metal was extracted from dolomite and magnesite on a large scale during World War II, but its recovery from these sources ceased in the following years. Deep-well magnesium brines in Texas were developed in 1970, and the brines of Great Salt Lake, Utah, were under development in 1972 by two companies for the recovery of magnesium compounds and the metal. Forsterite, the magnesium-rich variety of olivine, has been mined in North Carolina since 1933, and in Washington since 1956.

Since World War II, dolomite has provided the largest single source of magnesium-bearing compounds in the United States. More than 2 million short tons of dead-burned dolomite was produced annually in the midsixties, but changes in steelmaking reduced its consumption to 1 million tons in 1971; another several hundred thousand tons of caustic-calcined dolomite is used annually to precipitate magnesium hydroxide from sea water and brines. Reported production of magnesite reached a peak in 1956, when 690,000 short tons of crude magnesite was produced. Since then, production has not been reported, but in 1972 the Washington deposits were not mined, and therefore the production for that year was probably less than in 1969. About 1 million tons of brucite was mined from the Nevada deposits during 1934–66, but annual rates of production are not reported. Olivine production similarly is not reported but probably is on the order of several tens of thousands of tons per year.

Under categories currently reported by the U.S. Bureau of Mines, refractory magnesia sold and used by producers totaled 627,000 short tons in 1971 and 802,000 short tons in 1970; shipments of caustic-calcined and specified magnesias (exclusive of magnesia used in manufacture of the metal) totaled 102,000 short tons in 1971 and 122,000 short tons in 1970. Magnesium metal production was 123,000 short tons in 1971, continuing a rising trend of the previous several years. Figures on the amounts of magnesium compounds obtained from sea water, deep-seated brines, magnesite, and brucite are not available (Chin, 1971a, b).

Outside the United States, about 12 million tons of magnesite is mined annually; most is from deposits of crystalline magnesite, but more than 1 million tons is from deposits of bone magnesite. The consumption of bone magnesite has been increasing in recent years because this refractory possesses high strength and is resistant to high temperatures, properties desirable in the linings of basic-oxygen steel furnaces.

About 120,000 tons of magnesium metal is produced annually outside the United States. Rated capacity of plants recovering magnesia from sea water outside the United States totals 1.1 million

tons, and that of plants recovering magnesia from inland lakes, 200,000 tons (Industrial Minerals, 1970).

GEOLOGY

Magnesium is the eighth most abundant of the elements in the earth's crust; it averages 2.09 percent by weight of all igneous rocks. Magnesium makes up about 0.13 percent of sea water; during evaporation, it precipitates at an early stage, largely with carbonate minerals, but it also precipitates at the end stages, in bittern minerals. Magnesium carbonate also precipitates during evaporation from certain inland lakes.

MINERAL DEPOSITS

This chapter deals largely with resources of magnesite, brucite, and olivine; resources of dolomite, evaporite minerals, and brines are described elsewhere in this volume.

MAGNESITE

Magnesite occurs mainly in four types of deposits: as crystalline masses replacing dolomite, as impure crystalline masses replacing ultramafic rocks, as cryptocrystalline masses in ultramafic rocks, and as sedimentary beds and lenses.

Crystalline magnesite deposits in dolomite.—Accumulations of crystalline magnesite occur as massive lenses, stockworks, or disseminations in dolomite or in limestone locally altered to dolomite. Crystalline magnesite is light gray, gray, brown, pink, or red, and its grain size ranges from 0.5 to 20.0 mm. Its chief impurities are calcium, contained within the lattice of magnesite grains or within included dolomite grains; iron, contained either in breunnerite (ferroan magnesite) or as disseminated specularite; silica, as quartz veins or as impregnations of quartz and chalcedony; and silicate minerals such as talc, tremolite, anthophyllite, or enstatite, occurring in individual grains or in veins or lenses. Igneous dikes or stocks commonly cut magnesite lenses.

Crystalline magnesite deposits range in size from pockets containing a few tens of thousands of tons to irregular to lenticular bodies containing more than 100 million tons. Impurities may range from about 2 to 20 percent, excluding blocks rendered unminable by veins of silica or silicate minerals or by igneous dikes. Grade is as critical as size in determining the worth of any given deposit, particularly for magnesite used in the manufacture of high-purity refractories. There is little market for magnesite containing more than 4 percent CaO.

Only two districts in the United States contain large deposits of crystalline magnesite: one at Gabbs, Nev., and the other in Stevens County, Wash. Small occurrences are known in New Mexico and Texas (Vitaliano and Callaghan, 1956; Vitaliano and Cleveland, 1966; Schilling, 1968; and Bennett, 1941, 1943).

Crystalline magnesite deposits in ultramafic rocks.—Magnesite mixed with talc and with or without quartz occurs as lenses replacing dunite or serpentinized dunite. Deposits of this type are as variable in size as those in dolomite. They form massive lenses or occur as shells around ultramafic bodies. The only crystalline magnesite deposits in ultramafic rocks in the United States are found in north-central Vermont. These deposits consist of gray to faintly greenish gray rock, in which the magnesite occurs as grains or clusters of grains ranging from 0.01 to 30.0 mm in diameter in a matrix of fine-grained talc. Proportions of magnesite to talc in these deposits range from 38:62 to 50:50; the magnesite is low in lime but contains several percent iron; the rock as a whole also contains magnetite as an accessory mineral. A deposit near Timmins, in Ontario, Canada, contains 48–72 percent magnesite, 6–20 percent talc, and 11–21 percent quartz (Chidester, 1962; and Griffis, 1972).

Cryptocrystalline magnesite deposits.—Cryptocrystalline magnesite, also known as bone magnesite, occurs as nodules, veins, and stockworks in serpentinized zones of ultramafic rocks; it also is found as small deposits in tuffs. Bone magnesite resembles unglazed porcelain and generally is dead white but locally is tinted gray, green, or pink. Impurities include serpentine, enclosed in or bordering nodules and associated vein minerals, as well as opal, chalcedony, several hydrated magnesium silicate minerals, and rarely calcite or dolomite. Bone magnesite itself may contain traces to small percentages of lime and iron.

Bone-magnesite deposits tend to be much smaller than crystalline deposits; the largest group of veins in the United States, at Red Mountain, Calif., originally contained about 1 million tons of magnesite. Individual veins range from a few feet to hundreds of feet in length and depth, and from fractions of an inch to tens of feet in width. The wider veins tend to consist of separate magnesite nodules in serpentine.

Most bone-magnesite deposits occur in ultramafic rocks in California, but several are known in Oregon and Pennsylvania. Deposits of bone magnesite replace bedded rhyolitic tuff in eastern Nevada (Davis, 1957; Bodenlos, 1950a; and Vitaliano, 1951).

Sedimentary magnesite.—Sedimentary magnesite is a brown to gray carbonate rock which probably formed by evaporation. Individual beds may cover several tens of acres and range in thickness from inches to several feet. Such magnesite is interbedded with dolomite, clastic rocks, or strata of volcanic origin. Although the grade of some sedimentary magnesite is high, the thin beds cannot be mined economically. Deposits are limited to several States in the Southwest (Rubey and Callaghan, 1936; and Vitaliano, 1950).

PROSPECTING

Deposits of crystalline magnesite may be overlooked because magnesite differs from crystalline dolomite only slightly in luster and specific gravity. In some deposits, magnesite is more resistant to weathering than dolomite and hence forms bolder outcrops. Weathered surfaces may differ slightly in color from the weathered surfaces of dolomite. Talc-bearing crystalline carbonate rocks should be checked for magnesite, although talc also occurs in dolomite. Chemical or mineralogical tests thus may be needed to identify new prospects.

Crystalline carbonate masses in ultramafic rocks, particularly if mixed with talc, probably consist of magnesite; such material weathers shades of rusty brown owing to its contained iron.

Bone magnesite forms highly distinctive dead-white outcrops and float, perhaps associated with chalcedony and opal, which contrast like whitewash against the somber shades of the host ultramafic terrane.

Sedimentary magnesite perhaps is the most difficult type of magnesite deposit to recognize, because it has no clearly distinguishing physical features or characteristic geological associations.

GENESIS

Most carbon dioxide needed to form magnesite deposits probably was derived from deep-seated igneous sources, although some may have been furnished through thermal dissociation of underlying carbonate rocks; a very small amount may have been carried by ground water. Ultramafic rocks furnished the magnesia now found in their contained magnesite deposits, but the source of magnesia in crystalline deposits in dolomite is less certain. One hypothesis proposes that the magnesia was produced during thermal dissociation of underlying dolomite. Another hypothesis suggests that crystalline magnesite deposits are metamorphosed, recrystallized lenses of sedimentary magnesite, but this hypothesis does not explain the obvious replacement nature of many if not most crystalline deposits (Faust and Callaghan, 1948; Schilling, 1968; Vitaliano and Cleveland, 1966; Bodenlos, 1950a, 1954; and Lovering, 1969).

Sedimentary magnesite in the southwestern States formed in closed basins and therefore is of evaporite origin.

BRUCITE

Brucite [$Mg(OH_2)$] in minable concentrations rarely is found. Two such deposits are associated with magnesite at Gabbs, Nev.; there the mineral occurs as lenses of massive white to light-brown material resembling old-fashioned laundry soap, which is soft enough to scratch with the fingernail. Impurities include veinlets and grains of dolomite, magnesite, talc, forsterite, and periclase; the deposits also are cut by igneous dikes. The deposits lie close to a stock of granodiorite postdating magnesite deposition, suggesting that the intrusive locally drove off carbon dioxide in magnesite and formed magnesium hydroxide.

Besides the Gabbs occurrence, brucite has been found within the United States, in small amounts only in New Mexico (Schilling, 1968; Davis, 1957) and Arizona (Ericksen, 1969).

OLIVINE

Olivine [$(MgFe)_2\ SiO_4$] is a common mineral in quartz-free igneous rocks; its magnesium-rich variety, forsterite, forms the rock called dunite. Forsterite alters readily to serpentine minerals; thus, masses of fresh dunite are not common. Within the United States, fresh dunite makes up most of the Twin Sisters Mountains, east of Bellingham, Wash., and it occurs as smaller masses in North Carolina and Georgia (Stuckey, 1965; Moen, 1969).

OTHER SOURCES

Deep-well brines in Michigan and in other States have provided recoverable magnesium compounds, and the brines of Great Salt Lake are under development for the same purpose. (See "Evaporites and Brines.") Magnesium compounds are extracted from sea water in recovery plants on the Atlantic, Pacific, and Gulf coasts, the annual rated capacity of which in 1970 was 570,000 tons MgO. Dolomite is quarried in various States. Dolomite used to recover magnesium metal formerly was quarried in Connecticut, New York, Ohio, Michigan, Mississippi, and Washington. Deposits of evaporite minerals in New Mexico remain largely untapped as a source of magnesium-bearing compounds.

RESOURCES

IDENTIFIED AND HYPOTHETICAL RESOURCES

Magnesium resources in sea water are practically unlimited, and those in magnesium-bearing evaporites, dolomite, and dunite are enormous. Magnesium resources contained in interior saline lakes and seas must total billions of tons, and it is judged that deep-well brines contain large tonnages of magnesium salts. Identified resources in the magnesite deposits of the world total 12 billion tons; those in the brucite deposits of the world, several million tons.

The apparent reserve of magnesite of the United States in 1970 was placed at 65 million tons (Paone, 1970), about equal to the national reserve in 1960 (Comstock, 1963). Data are not available to determine what fractions lie in recoverable and subeconomic resources, but probably less than half of the identified resource is commercially recoverable under present prices and required grades. Hypothetical resources are limited to unexplored magnesite at depth below known deposits. Perhaps 20 million tons of subeconomic resources seems a reasonable estimate.

Recoverable resources of magnesium chloride in Great Salt Lake are said to exceed 600 million tons. Resources of fresh dunite in Washington State total billions of tons, and those in North Carolina total more than 200 million tons. Recoverable resources of brucite remaining in the Nevada deposits are said to be small, probably not more than 1–2 million tons. At least an additional several tens of millions tons of magnesite constitutes a subeconomic resource within the magnesite-talc deposits in Vermont.

A recent compilation set the apparent world reserve of magnesite at 9.4 billion tons, exclusive of small reserves in several countries (Paone, 1970). To this should be added 300 million tons of crystalline magnesite in Brazil (Bodenlos, 1950b, 1954); 240 million tons of magnesite in the Sudan (Whiteman, 1971); 100 million tons of magnesite in Canada, which consist of magnesite-talc-quartz rock replacing dunite; and 2,000 million tons of talc-rich magnesite at Savinsk, in eastern Siberia, the host rock of which is unreported (Industrial Minerals, 1970). Total identified resources consist largely of crystalline magnesite associated with dolomite; but at least 1 billion tons consists of crystalline magnesite replacing dunite, and perhaps more if the Siberian occurrence lies in such rock. Identified resources of bone magnesite are not well known, but older compilations indicate that they are on the order of several tens of millions of tons. Notwithstanding, bone magnesite is at present being mined at a rate of more than 1 million tons per year, so it is likely that past resource estimates of bone magnesite were conservative.

Although magnesium-bearing evaporite minerals are not covered in this chapter, the tachyhydrite deposits of Sergipe, Brazil, must be cited as a large new resource; R. J. Hite reported that the upper zone alone contains about 4 billion metric tons of the mineral, equivalent to 380 million tons of magnesium metal (U.S. Geol. Survey, 1970, p. A216; Wardlaw, 1972). Similar deposits also have been found in Gabon and Zaïre, Africa. Tachyhydrite ($CaMg_2Cl_6 \cdot H_2O$) is so soluble, even in drilling brines, that its occurrence may have been overlooked in other evaporite sequences.

SPECULATIVE RESOURCES

Crystalline magnesite deposits are not common. Areas favorable for their occurrence are carbonate rocks near igneous intrusions, which in the United States were thoroughly searched without success during World War II. Probably nearly all deposits of crystalline magnesite in Europe have been found, but undiscovered deposits undoubtedly exist on other continents. Because such deposits tend to be large, any one discovery could add from tens to hundreds of millions of tons to the world's resources.

Crystalline and bone magnesite deposits in ultramafic rocks are globally widespread. Bone magnesite outcrops are conspicuous; therefore, most near-surface deposits probably have been found, even in remote areas. Ore bodies undoubtedly exist that do not crop out; targets for exploration should include serpentinized shear zones in relatively unaltered masses of peridotite, particularly where the serpentine is veined by chalcedony or opal. Deposits of crystalline magnesite in ultramafic rocks evidently are very rare, but most seem to be very large although low in grade. Undoubtedly more will be discovered in those parts of the world not yet fully geologically mapped.

PROBLEMS FOR RESEARCH

Industrial technology successfully developed methods to recover magnesium-bearing compounds and the metal from a wide variety of natural resources. Efforts are continuing to produce stronger refractories, to increase the efficiency of recovery processes, and to develop new magnesium-bearing alloys.

The geology of magnesium-bearing mineral deposits is reasonably well known. Not enough is known, however, about the genesis of deep-seated magnesium-rich brines. The world's resources of

bone magnesite should be reappraised in view of current demand for that raw material as a dead-burned refractory.

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MANGANESE

By John Van N. Dorr, II, Max D. Crittenden, Jr., and Ronald G. Worl

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ABSTRACT OF CONCLUSIONS

Known minable reserves and known resources of manganese are very large in relation to world consumption but are very irregularly distributed throughout the world. The United States has virtually no domestic reserves and its known resources are both very low grade and refractory to economic concentration. The principal hopes of finding domestic reserves or resources of conventional types may lie in (1) finding the source of the manganese of the Pierre Shale, conceivably buried under Pleistocene sedimentary rocks in central or western Minnesota or adjacent areas; (2) finding another Molango-type deposit by careful analysis of the distribution of manganese in certain miogeosynclinal carbonate rocks; or (3) finding the source of the high manganese concentrations in the Salton Sea brines. Much more promising modes of relieving dependence on foreign sources are by vigorously attempting to perfect techniques of effectively exploiting sea-floor nodules and by dissolving legal impediments to large-scale investment in subsea mining. Maintenance of an adequate national stockpile is essential.

With respect to world resources, efforts should be made to explore the sedimentary high-grade manganese carbonate bodies, which through weathering have given rise to overlying rich supergene oxide deposits, in order to establish the tonnage and grade of material that will be available for use when oxide deposits are depleted; the tonnage is probably great. There is some possibility that deposits without the oxidized cap might be found in eugeosynclinal belts in the North American Shield areas.

INTRODUCTION

Manganese, a metal rarely seen in elemental form, is essential in two ways to the manufacture of steel: (1) used as a scavenger in molten steel, it combines with sulfur and oxygen, which make steel brittle, and removes them as part of the slag; (2) used as an alloy, it makes steel more resistant to shock or abrasion. It is used also in the chemical industry and, in dioxide form, as a depolarizer in dry batteries. More than 90 percent of the consumption in the United States is by the steel industry, and no substitute has yet been found despite much effort. About 13–20 pounds of manganese is consumed per ton of steel manufactured; therefore the element is essential to

the whole industrial capacity of the world. When we can do without steel, we can do without manganese.

Manganese is introduced in the steel-making process primarily as the alloy ferromanganese (about 78 percent Mn, 15–18 percent Fe), as spiegeleisen (about 15–20 percent Mn, the rest largely Fe), as silicomanganese (about 66 percent Mn, 12–20 percent Si), or as manganese metal added to the converter of whatever type may be used or to the ladle. Ferromanganese, which accounts for more than 75 percent of consumption, is made by smelting an ore with a Mn/Fe ratio of 7:1 or greater. For a succinct discussion of the consumption, uses, and processes involved in the manganese industry, the reader is referred to the manganese chapter in the U.S. Bureau of Mines publication "Mineral Facts and Problems" (Sheridan, 1970).

The United States is now completely dependent upon foreign sources of manganese, for the last domestic manganese mine closed in 1970.

Salient data from U.S. Bureau of Mines Minerals Yearbooks on domestic and world production of manganese ores and domestic consumption of ferromanganese and imports of these materials are given in table 74.

TABLE 74.—*Production, imports, and consumption of manganese ore and concentrates and ferromanganese, 1966, 1970, and 1971, in millions of short tons*

	1966	1970	1971
Ore and concentrates:			
Domestic production, >35 percent Mn	0.014	0.005	0
World production, >30 percent Mn	19.1	19.2	20.4
Imports, >35 percent Mn	2.6	1.7	1.9
Ferromanganese:			
Domestic consumption	1.0	1.0	.9
Imports for consumption	.25	.29	.24

Principal suppliers of manganese ore to the United States in 1971 were (in order of importance): Brazil, Gabon, Republic of South Africa, Zaïre (ex-Kinshasa Congo), and Ghana. Principal suppliers of ferromanganese were the Republic of South Africa, France, and India, in that order. In 1970, manganese ore was produced by 40 countries, of which 11 produced 96 percent, six produced 84 percent, and three produced 63 percent. With the exception of a few hundred tons of ferromanganese imported from Yugoslavia, none of the U.S. manganese supply in 1971 came from the socialist countries.

EXPLOITATION

The necessity for manganese in the steel-making process to avoid brittleness in the steel was recognized in 1856 by Mushet, whose discovery made the Bessemer converter practical. Since then, increasing world production of manganese has closely paralleled that of steel. In the middle of the 19th century, the United States was largely self-sufficient in manganese. Major deposits were found in the U.S.S.R., Brazil, and India in the late 19th century, and large deposits were found in Africa, Brazil, Cuba, and Mexico in subsequent decades. The most recent significant discoveries were those in Amapá, Brazil (>30 million tons), and the Kalahari basin, South Africa (>3,000 million tons), in the 1940's, in Gabon (200 million tons) in the 1950's, and at Groote Eylandt in Australia (about 75 million tons) in the 1960's; the carbonate deposits of Molango, Mexico (>15 million tons), were also discovered in the 1960's. Despite unparalleled consumption since World War II, known reserves of commercial-grade ore are now far greater than at any time in the past; the grade of the ore used is nearly as high as it ever was, and the price is lower in constant dollars than for many years.

Production from various sources in the United States in the 20 years from 1943 to 1963, the period of maximum production, is shown in figure 45. It should be remembered that the curve entitled "Low-grade purchases for stockpile" represents noncommercial manganiferous material, most of which contained 15–17 percent manganese, that was then and is still unusable as a source of manganese without concentration. This production, the carlot purchases,

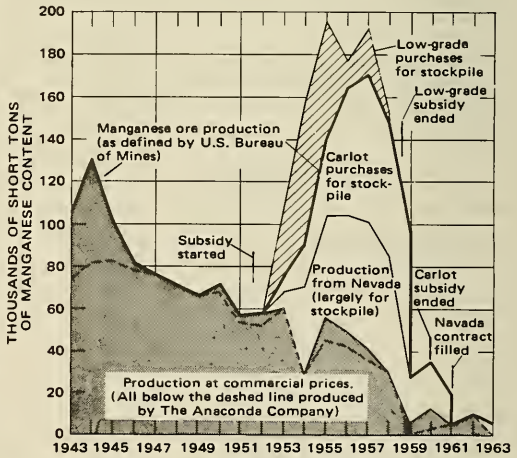

FIGURE 45.—Domestic manganese ore production (metallurgical grade), 1943–63, distributed according to sources of output. Modified from Brooks (1966, p. 75).

and the Nevada production for stockpile, the latter two of commercial grade, were heavily subsidized. The declining production before the subsidy ended clearly indicated that most known deposits were uneconomic even at the subsidized prices. No important domestic discoveries have been made since, and domestic production since 1963 has been very small, largely from Montana and New Mexico.

Much metallurgical research has been done in the United States and Canada to make feasible the extraction of manganese from the low-grade ores of those countries and from slag piles from open-hearth furnaces; techniques are available to do this at a price two to five times the present world price for manganese.

Most manganese ore now produced in the world comes from large open-pit mines; underground mines still produce in countries with low wage scales or where the ore zone is thick, permitting efficient underground operation, as at Molango, Mexico, and in the Chiatura field in the U.S.S.R. Mining methods are standard. Concentration in most areas consists of relatively simple washing, screening, or jigging to remove clay, sand, or other contaminants. Hand sorting, however, still exists in some mines in South Africa and India. The first pelletization plant for fine ore is scheduled to begin producing in Brazil in 1972; heretofore such fine material has been stockpiled, sintered, nodulized, or discarded, as lumpy ore is needed in ferromanganese production.

Except for the manganese carbonate mines in Montana and a few small mines in the Western United States in which base or precious metals were coproducts or in which the manganese was a byproduct, most manganese mines are exploited only for that metal. In the future, when the mining of manganese nodules from the sea floor becomes technologically and economically feasible, copper, nickel, and cobalt will certainly be produced as well as manganese. Extraction of the valuable metals would probably be by hydrometallurgical and electrolytic techniques.

As in all mining operations where there is no legal obligation or economic stimulus for preservation of the environment, manganese mining results in mine dumps, tailings piles, rapid erosion of mined-out areas, and large pits. Except for increased sediment load and siltation, manganese mining does not cause water pollution.

The only environment-restoration effort seen by the senior author in visits to hundreds of manganese mines on four continents was being carried on at the enormous Nikopol open-pit mines in the U.S.S.R. There the rich black topsoil of the Ukraine was carefully removed, the sterile rock overburden replaced after the underlying manganese bed had been extracted, and the topsoil replaced. After 3 to 4 years, orchards or grain were planted and seemingly throve. Lakes, which had been landscaped, had formed in some of the older unrestored large pits. Clubhouses had been built, and the lakes were used for outboard motorboats, water sports, and fishing by the miners and their families. *Thus, the land was withdrawn from productive agriculture only for about 5 or 6 years and theretofore-absent recreational facilities were developed.* Well over 100 million tons of material is moved each year in these mines. The geology of the Nikopol area makes such restoration relatively easy, and the fertility of the soil makes restoration economic for an integrated economy.

The reduction of manganese ore to ferromanganese is commonly accompanied by much air pollution unless special equipment is installed to prevent this. Fumes high in MnO_2 are said to be very toxic and to cause a high incidence of respiratory disease.

Extraction of deep-sea nodules should cause little if any significant damage to the envidonment; in fact, the bottom water that is brought to the surface in hydraulic mining is higher in nutrients and will support a more numerous and broader flora and fauna than the surface water. Properly planned hydrometallurgical extraction should cause no serious pollution problems.

GEOLOGIC ENVIRONMENT

GEOCHEMISTRY AND CRUSTAL ABUNDANCE

Manganese (Mn) constitutes about 0.1 percent of the earth's crust and is the 12th most abundant element. It is more abundant in mafic rocks, averaging about 0.16 percent, and less abundant in granitic rocks, averaging perhaps 0.06 percent. Deposits that were economic at 1971 prices contained between 25 and 50 percent manganese; thus the element must have been concentrated by natural processes 250–500 times the normal background to form an economic ore deposit.

The geochemical characteristics of manganese are very similar in many ways to those of iron; therefore some manganese deposits are closely related to iron deposits, and some contain considerable quantities of iron.

Manganese commonly occurs in nature in three valence states: $+2$, $+3$, $+4$. The ionic radius of bivalent manganese is close to that of bivalent iron and calcium; manganese ions may substitute for iron ions in ferrous minerals. Indeed, almost all the

manganese in igneous rocks occurs in such diadochic substitutions, largely in mafic minerals. True manganese minerals are most rare in such rocks. Mafic minerals break down readily under weathering, and the contained ionic manganese is liberated. Under reducing or near-neutral conditions, bivalent manganese is relatively soluble and is commonly transported by subsurface or surface waters to sites where for some reason the waters have higher oxygen content. There the mnaganese may be deposited at higher valences in the relatively insoluble oxide form. Given proper conditions, the manganese may also be deposited in bivalent carbonate form. Bivalent manganese may also substitute for the calcium ion in limestone or dolomite, forming manganoan limestone or dolomite or deposits of even more complex manganiferous carbonate minerals.

Volcanic rocks subjected to large-scale alteration, such as molten lava extruded into relatively shallow sea water or solid volcanics altered by hydrothermal solutions, may also lose considerable quantities of manganese by destruction of mafic minerals. The manganiferous solutions may then transport the manganese to sites where the ambient conditions abruptly change because of variations in wallrock, redox potential, intermixing ground water, rapid cooling, or other factors. There the manganese may be precipitated in veins, replacement deposits, or hot-spring deposits, or, in marine or lacustrine basins, as sedimentary deposits.

Manganese derived from cooling magma tends to concentrate in pneumatolytic and hydrothermal solutions. Pegmatites locally contain a widely varying suite of complex manganiferous minerals of no economic interest as a source of manganese. In veins and replacement deposits of magmatic origin deposited at relatively low temperatures, manganese as the carbonate or silicate may replace wallrocks or form the gangue of precious- and base-metal deposits, as at Leadville, Colo., Pioche, Nev., and Philipsburg, Mont. In many localities the manganese occurs in zones outside the main center of base- or precious-metal deposition. The manganese so deposited may be produced as a byproduct or coproduct of the base-metal mining, as at Butte, Mont. Low-temperature veins of manganese oxide are also formed from such solutions, but these are of minor economic significance.

Manganese may be carried to lakes or the sea in ionic solution or in colloidal or very finely particulate form. Certain bacteria precipitate manganese as part of their life cycle, and bog and some lake deposits apparently are due to such organic action. Other lake or basin deposits are apparently due to sudden increases in the oxygen content of the water, typically in near-shore environments, resulting in long narrow deposits of manganese oxides closely related to facies changes of the host sedimentary rocks. Manganese that reaches the sea may be deposited in a platform or near-shore environment, either as rather pure manganese oxide mixed to a greater or lesser extent with detrital terrigenous sediments, or as manganese carbonate or complex manganese-calcium-magnesium carbonate minerals if the environment is more reducing.

The exact environmental conditions causing the deposition of such sedimentary manganese in any particular spot have never been satisfactorily explained. We know the general mechanism and environment of deposition but not the localizing factors; that is, we often know how a deposit was formed but not why it was formed in a particular spot and not in some other spot. This is a critical question for the economic geologist.

Many deposits of sedimentary and other origins are in rocks later subjected to metamorphism. If the original deposits are relatively pure oxides or carbonates, they remain generally unchanged; if intermixed alumina and silica are available, the original manganese reacts with them to form bodies of recrystallized manganese oxide or carbonate with some intermixed manganiferous silicates. Examples are the oxide deposits of the Central Provinces of India and the manganese carbonate bodies of Ghana and Brazil. If the original deposit is high in intermixed alumina and silica, all the original manganese carbonate or oxide reacts with the impurities to produce extensive zones of manganese silicates, called gondite, useless for industrial purposes and from which only small and low-grade secondary deposits form.

In the deep sea, and locally at the intermediate depths, where sedimentation of detrital and organic material is very slow, nodules containing from about 10 to 35 percent manganese and from 5 to 35 percent iron cover extensive areas. Some believe that most of the manganese in these nodules is derived ultimately from terrigenous sources; others believe that contributions from submarine volcanic activity are large. The manganese in these nodules commonly occurs as complex oxide minerals. These nodules may be the ultimate sink for the manganese and iron and some other metals introduced into the sea water from rivers and submarine volcanics. Their equivalent has not been recognized in land deposits, but their included metals may be recycled as sea-bed deposits which are carried to great depths in the mantle in subduction zones and there are melted to

form new igneous rocks with associated ore bodies, completing and renewing the geochemical cycle. Thus may be explained the association of volcanogene manganese with volcanic rocks ringing the Pacific.

To summarize, the manganese in the earth's ore deposits originated from manganiferous mafic minerals in igneous rocks or from magmas, being released by weathering and hydrothermal alteration of those minerals or by fluids driven off from the crystallizing magma. The manganese was carried to the site of deposition in very dilute solution and was there deposited in significant concentration because abrupt change of the environment rendered the dissolved manganese insoluble. Changes in the oxidation-reduction potential were probably the most important control in the precipitation of manganese. There is reason to believe that biologic agents were involved in deposition of major carbonate-facies manganiferous sedimentary deposits, but there is no evidence of this for major oxide-facies deposits.

Much disagreement exists as to the relative importance of the various sources of manganese discussed above; the enormous size of the major sedimentary deposits strains the capacity of direct contribution from volcanic or magmatic sources. The lack of volcanic rock closely associated with such major deposits makes the weathering of igneous rock a more likely source of manganese for the larger deposits. The manganese in the higher grade deposits has in many instances been through at least two stages of natural concentration: (1) its original deposition and (2) subsequent weathering of low grade deposits, particularly the carbonates, that removed dilutents.

TYPES OF MANGANESE DEPOSITS

Primary manganese deposits may be classified into three types—sedimentary (including sea-floor nodules), volcanogene, and hypogene—that to some extent are intergradational. All are modified to greater or lesser extent by supergene processes; in oxide form, manganese is less soluble than many other elements and is concentrated in the zone of weathering.

MANGANESE MINERALS

Table 75 shows the more common manganese minerals formed in these various environments.

SEDIMENTARY DEPOSITS

A distinction must be made between sedimentary deposits of manganese laid down as carbonates and those deposited as oxides. In all instances for which data are available, major deposits of high- and medium-grade primary manganese carbonate are known to be closely associated with carbonaceous or graphitic rocks, often rather clayey, indicating a strongly or moderately reducing sedimentary environment, in many examples in closed basins. Primary oxide deposits, on the other hand, are more commonly associated with coarser clastic sediments with little or no free or organic carbon, indicating nearshore and strongly oxidizing conditions with relatively free circulation of water. The Ukrainian deposits in the U.S.S.R. are unique in that the intertonguing transition from oxide facies to carbonate facies can be observed to occur basinward over distances ranging from some hundreds of meters to a few kilometers. In Precambrian and lower Paleozoic rocks, sedimentary manganese deposits may be closely associated in space and time with iron-formation; oxide-facies manganese deposits may be interbedded with oxide-facies iron-formation, whereas the carbonate-facies deposits tend to be separated stratigraphically (as at Moanda,

TABLE 75.—*Common manganese minerals*

[Supergene mineralogy essentially the same regardless of type or origin of protore except possibly nsutite]

Supergene minerals

Pyrolusite [1]	Birnessite [1]
Cryptomelane [1]	Todorokite [1]
Psilomelane [1]	Chalcophanite [2]
Coronadite [1]	Manganite [2]
Nsutite [1] (carbonate source)	Lithophorite [2]

Metamorphic minerals

[Metamorphic mineralogy is largely dependent on metamorphic grade and rock composition. Many oxides and rhodochrosite remain intact during metamorphism in environments low in Al and Si. Many primary oxides stable in low-grade metamorphism])

Manganite [2]?	Rhodochrosite [4]
Bixbyite [3] (all grades)	Rhodonite [5]
Braunite [3] (all grades)	Spessarite [5]
Hollandite [3] (all grades)	Tephroite [5] (higher grades)
Hausmannite [3] (higher grades)	Other Mn silicates [5]
Jacobsite [3] (higher grades)	

Hypogene Minerals

Pyrolusite [1]	Jacobsite [3]
Cryptomelane [1]	Hausmannite [3]
Psilomelane [1]	Rhodochrosite [4]
Birnessite [1]?	Mn-Fe-Mg-Ca carbonates
Coronadite [1]	Black calcite [4]
Hollandite [3]	Rhodonite [5]
Braunite [3]	

Volcanogene minerals

Pyrolusite [1]?	Mn-Fe-Ca carbonates
Psilomelane [1]?	Neotocite [5]
Braunite [3]	Bementite [5]
Hausmannite [3]	Mn silicates
Rhodochrosite [4]	

Sedimentary minerals

Pyrolusite [1]	Braunite [3]
Cryptomelane [1]	Rhodochrosite [4]
Psilomelane [1]*	Mn-Fe-Mg-Ca carbonates
Birnessite [1]*	Black calcite [4]
Todorokite [1]*	Mn in lattice of magnetite and
Manganite [2]	Fe silicates and carbonates

[1] Higher oxide.
[2] Hydroxide.
[3] Medium and lower oxide.
[4] Carbonate.
[5] Silicate.
[6] Other.
* Nodule minerals.

Gabon) or spatially (as in Minas Gerais, Brazil) from the (usually) carbonate-facies iron-formation.

Most large sedimentary deposits of manganese were deposited in sea water, as indicated by fossils and associated rocks. Many smaller deposits, generally oxide facies, were formed near the shores of fresh-water lakes, as indicated by fossils (Autlan, Mexico, and some deposits in Chile). Some sedimentary manganese oxide deposits are closely associated with gypsum and may well have formed near the shores of closed evaporite basins (Three Kids, Nev.; Lucifer, Mexico; and possibly some Chilean deposits).

The most favorable host rocks for carbonate-facies sedimentary manganese deposits seem to be eugeosynclinal sediments with associated tuffaceous and limy rocks or platform limestones or dolomites, deposited in local sea-floor depressions. The deposits in the eugeosynclinal sediments are commonly composed of rhodochrosite and to varying degrees are diluted by clastic rocks, whereas those deposited with platform or miogeosynclinal carbonates commonly contain manganoan calcite or dolomite or complex calcium-magnesium-manganese carbonates and are rarely diluted by clastic sediments. The large deposits of very low grade manganoan carbonate rock, containing from half a percent to a few percent manganese, are commonly miogeosynclinal or platform deposits and do not characteristically contain free carbon. Carbonate-facies iron-formation may locally contain several percent manganese, probably present as manganoan siderite.

Sedimentary deposits are characteristically stratiform and have widely varying degrees of lenticularity. In many places, particularly the oxide deposits, these lenses are much longer than wide. Some extend for many kilometers, as in the Ukraine and in the Kalahari Basin, South Africa, but more commonly the lenses are a few hundred meters to a few kilometers long and a few tens of meters to a kilometer or more wide. In many deposits the manganese is in a single bed; in others, such as Chiatura, U.S.S.R., and Urucum, Brazil, the manganese is in several separated beds. Thickness of the beds ranges from a hairline to about 30 meters; except in the Kalahari field, few ore-grade primary oxide beds are more than 3 meters thick. High-grade carbonate beds tend to be thicker but to be smaller in areal extent. Low-grade manganoan dolomite or limestone may be very thick and very extensive.

The grade of the sedimentary manganese deposits also varies widely. Few unenriched oxide beds contain more than 50 percent Mn; more contain between 40 and 50 percent, and probably most contain between 25 and 40 percent Mn before beneficiation. Few beds containing less than 25 percent Mn are now mined. The carbonate beds are lower grade because manganese carbonate contains only 47.8 percent Mn at theoretical purity, which is rarely found; 35 percent Mn is considered to be high grade for manganese carbonate in place, and most beds contain between 15 and 30 percent Mn.

Workable sedimentary manganese oxide deposits range upward in size from a few tens of thousands of tons. There are many such deposits with less than a million tons, a substantial number with reserves between 1 million and 10 million tons, several with reserves between 10 million and 200 million tons, and three known areas with even larger reserves, ranging into the billions of tons. The Ukranian and the Kalahari deposits each are known to exceed 3 billion tons, and indications are that they may be several times this size, there is no economic incentive to prove such larger reserves.

No really large deposits of carbonate-facies manganese ores of ore grade are now known, but exploration of such bodies has rarely penetrated far below the zone of weathering, and this resource is poorly known. High-grade oxide ore resulting from the weathering of such beds rarely occurs in bodies of more than 50 million tons, the most productive districts being the Nsuta deposit in Ghana, the Serra do Navio deposits in Amapá and the Meridional deposits in Minas Gerais, Brazil, and the Kisenge deposits in Zaïre. The Moanda deposit in Gabon, by far the largest of this type yet discovered, has reserves of about 200 million tons of high-grade secondary oxide ore. In many but not all such deposits, it may be presumed that the resource of unaltered manganese carbonate at least equals the tonnage of oxide formed from it.

MANGANESE NODULES

An enormous potential future source not only of manganese but also copper, cobalt, and nickel is on the ocean floors in the form of discrete nodules, locally welded together to form a pavement. Despite much research into the nature, composition, and distribution of these nodules, particularly since sophisticated cameras and light sources permitted photographing the sea floor, our knowledge of this resource is in its infancy. In the last decade several tens of millions of dollars have been spent by industry and some governments in locating favorable areas and in an attempt to develop modes of submarine mining and extraction of the valuable metals from the nodules. Within a decade or less, if political obstacles can be overcome, economic extraction

might well become practical. Several major American and foreign companies and governments are now engaged in scientific and technological research toward this goal.

Extensive areas of the ocean floor have concentrations of nodules that range from a few millimeters to several tens of centimeters in diameter and are roughly spherical to ellipsoidal. The nodules are composed of roughly concentric layers of material of varying composition, largely oxides of iron and manganese, deposited around nuclei of broken nodules, fragments of volcanic ejecta or other clastic material, and, rarely, fossils. It is estimated that these nodules grow at the rate of 1–5 mm per million years.

Nodules are most abundant and highest in tenor in parts of the oceans that receive minimal contributions of sediments; these are the deeper parts, ranging from about 2,500 meters to about 6,000 meters in depth. Lower-grade deposits are found in great abundance on the Blake Plateau, off Florida, at much shallower depth. Although nodules buried in the sediments of the bottom are found, the first 30 cm down from the interface is believed to contain about 65 percent of the useful material; the deposits should be envisioned as very widespread but very thin accumulations of consolidated nodules resting in and on a usually unconsolidated and very fine clay matrix.

The metallic content of the nodules varies widely from ocean to ocean, regionally and to some extent systematically within the individual oceans, and from place to place within the regions. Variations in nodule population may be very abrupt. Various authors have presented generalized information on composition and population, but the detailed data on which mining plans and resource calculations can be based, resulting from prospecting in progress, are not publicly available. It is understood, however, that areas, each of 2,600 square kilometers or more, have been located in which the nodules average more than 25 percent Mn, 1.0 percent Cu, 1.0 percent Ni, and 0.25 percent Co, with smaller values in other metals. The iron is not economically recoverable. At 1972 prices, the value of the metals in such nodules would be more than $150 per dry ton. The richer areas may contain about 13,500 tons per square kilometer or even much more; the average in deposits of minable size would probably be significantly less. Although astronomical figures as to the total tonnage of nodules on the sea floor have been published, resources in areas having a minable population of nodules are probably far less, but still undoubtedly very large. Extraction of the metals from the nodules demands innovative metallurgical practice; dredging of the nodules from great depths demands innovative mining practice.

The genesis of these manganiferous nodules is hotly debated. Some oceanographers believe that the metallic content is derived from submarine volcanism or alteration of submarine volcanic rocks; others, that it comes from reactions in the upper part of the sediments by which the metals are released during diagenesis of the sediments; and still others, that the metals are derived by subaerial weathering of the continental masses, being transported to the ocean basins by rivers, and to the sites of deposition by ocean currents. The presence of extensive deposits on the Blake Plateau on a limestone substrate, far from volcanic activity, suggests the third theory as the preferred model there. However, a sole source for all the deposits does not seem required.

VOLCANOGENE DEPOSITS

Because many small-scale and some medium-scale deposits of manganese are closely related in space and time to volcanism, the conclusion that such deposits are somehow genetically related to volcanism seems unavoidable. There is no general agreement as to the mechanism by which the manganese has been separated from the volcanic material and concentrated; several processes may be involved. This uncertainty, as well as the wide variation in types of deposits (ranging from clearly sedimentary to vein-type deposits) that are closely related to volcanism, makes use of the term "volcanogene" appropriate. This type of deposit is gradational both with the sedimentary type already discussed and with the hypogene type discussed below, and no clear-cut separation can be made.

Volcanogene deposits are closely associated with volcanic rocks, of both pyroclastic and flow origin, and either subaerial or submarine. In many instances the pyroclastic rocks have been deposited in lakes or the sea and are closely associated with clastic and chemical sediments or with limestone.

Major volcanic piles, such as those in eastern Cuba or the Olympic Peninsula in Washington, are favored sites for this type of deposit. Peculiarly, although such piles may have a maximum thickness of thousands of meters, the manganese deposits in many of them are confined to widespread zones a few meters to a hundred meters thick, indicating that the concentration of manganese by volcanic processes or from the volcanic rocks was not a continuing and normal process but demanded special conditions, the nature of which remains uncer-

tain. The depth of the water into which submarine volcanics were extruded may be one governing factor, for below a certain depth the confining water pressure is so high that included volatiles in the molten lava cannot readily escape.

Because many volcanic piles and extensive areas of volcanic rock contain no concentrations of manganese, the mere presence of volcanic rocks is no indicator of potential manganese discoveries. Characteristically, however, if one manganese deposit is found in such rocks, many others will be found in the same general area. Commonly, one or two deposits will be much larger and (or) higher grade than the others. Although deposits are known from continental volcanic rocks, the more important deposits are found in a marine or lacustrine environment, as in Mexico, Chile, and Cuba, and thus are really sedimentary deposits, in the strict sense of that term.

Volcanogene deposits are commonly but not exclusively composed of the oxide minerals, and the mineralogy is usually somewhat more complex than that found in unmetamorphosed sedimentary deposits without volcanic affiliation. Replacement of the diluting clastic and pyroclastic fragments in the ore horizon by manganese minerals is common; this seems to be a diagenetic feature in many places but may also be the result of supergene or hypogene alteration. In many such deposits, chert in small to rather large lenses accompanies, underlies, or overlies the manganiferous material, which here may be the hydrous manganese silicates bementite and neotocite. These manganese silicates are not ore minerals.

Deposits large enough to be economically interesting are commonly either sharply lenticular or stratiform; the larger ones are stratiform. Numerous but normally very small deposits may be associated with altered volcanic rocks and spilites. The volcanogene deposits interfinger with tuffaceous and (or) calcareous sediments or cherty and jaspery rocks. Local unconformities and abrupt lithologic changes in the host rocks are common.

Reserves in volcanogene deposits are characteristically small to medium in size. Very few deposits contain more than a million tons of recoverable ore, the largest probably being the Charco Redondo deposit in Cuba, which has produced about 5 million tons, and the Autlan deposits in Mexico, which produced about 4 million tons before exhaustion. Both are stratiform deposits.

With some notable exceptions, such as the Crescent mine in the Olympic Peninsula, most such deposits are medium grade, and the ore must be concentrated before shipment.

As with many other types of ore deposits, the localization of volcanogene deposits is apparently caused by relatively abrupt and localized changes in the nature or environment of the fluids which brought the manganese to the site of deposition. For deposits such as those in the Olympic Peninsula, the interface between the hot lava and the sea water into which it was extruded was the site of an abrupt change, and the manganese was deposited at and near that interface. For deposits such as Charco Redondo, the manganese evidently was transported some distance and deposited in a sedimentary environment with limestone and waterlaid tuff.

The sources of the manganese deposited in such bodies may be either fluids evolved from the magma at depth during volcanism, or, in small deposits such as those in the Olympic Peninsula, perhaps the alteration of the rock as it reacted with the sea water.

HYPOGENE DEPOSITS

Myriad small and a few medium-sized deposits of manganese ores are of hypogene origin—that is, they were deposited directly from warm fluids rising from sources deep in the earth. Some of these deposits merge into the volcanogene type, and it is impossible to be sure how closely they are related genetically to the volcanic rocks that enclose them. They also merge into the sedimentary type in that the fluids that brought the manganese into the basins in which sedimentary ore deposits formed by the normal sedimentary processes are thought, in some instances, to have been thermal waters.

The hypogene deposits occur in the same structural setting as the base- and precious-metal deposits with which they are often associated. Most are related to intrusive rocks, about which they are zonally arranged. They may take the form of veins, as at Butte, Mont., or replacement deposits in limestone or dolomite, as at Philipsburg, Mont. Another type, more abundant in the Basin and Range province of the United States and Mexico, is the vein deposit, predominantly in volcanic rocks. A few minor deposits are in the aprons of hot springs.

Most of the vein deposits formed at relatively low temperatures. In most, the manganese is in oxide form, but in a few it is in carbonate form. The few known occurrences of manganese sulfide are typically in veins. The replacement deposits may be in either oxide or carbonate form; carbonate deposits have commonly been oxidized at and near the surface by supergene action.

Few vein deposits have been followed to consid-

erable depths; nearly all die out or change their nature at depths of a few tens of meters to a few hundred meters. Many veins reveal strongly increasing percentages of hematite or barite with depth, indicating a zonal pattern. A number of deposits in brecciated volcanic rocks consist of myriad small thin veinlets of nearly pure manganese oxide lining fractures in the host rocks.

Replacement deposits of manganese carbonate are commonly in limestone or dolomite and tend to form tabular or pipelike shoots and irregular pods adjacent to faults or other conduits by which mineralizing solutions gained access to host rocks. Permeability of the host rock is a major control; therefore brecciated zones are favored. Replacement on a large scale is apparently confined to the more calcareous rocks, although tuffaceous rocks are replaced locally. Hypogene manganese oxide deposits are more generally confined to veins, generally filling fissures but in some instances replacing fault gouge, breccia, or other particularly permeable zones in host rocks of various types.

The vein deposits of manganese in the United States, Mexico, and Morocco have yielded a small tonnage of relatively high grade ore for many years. Locally such ore is rather low grade in the vein but can be hand sorted or mechanically concentrated to bring it to merchantable grade. Few such deposits yield as much as 100,000 tons; most contain a few tens to thousands of tons of salable ore. The replacement deposits may be much larger but generally are lower in grade, as at Leadville, Pioche, and Philipsburg.

The hypogene ores are deposited from thermal fluids originating at depth in the earth. Undoubtedly some of these fluids are derived from crystallizing magma; others are probably heated ground waters that derived their metallic content while circulating through and altering preexisting rocks of diverse origin. As the fluids approach the surface, changes in their environment and chemistry make the manganese insoluble and it deposits on the conduit walls or, if the chemistry is favorable, replaces the wallrocks. Experience has shown that there is little likelihood of finding significant hypogene oxide deposits at depths of more than a hundred meters or so; carbonate deposits may be found at greater depths, usually associated with deposits of other metals.

RESOURCES

IDENTIFIED AND HYPOTHETICAL RESOURCES

There is no lack of identified manganese resources in the world today, but these resources are so distributed that only one industrialized country, the U.S.S.R., is not almost completely dependent on imports for its supply. Table 76 gives the general

TABLE 76.—*World manganese ore resources, in millions of tons*

Country	Reserves [1]	Conditional resources [2]	Hypothetical resources [3]
North America:			
Canada	0	195	-----
Cuba	1(?)	3(?)	-----
United States	0	961	100(?)
Mexico	15±	50±(?)	200(?)
North America, total	16±	1,210±	300(?)
Africa:			
South Africa	3,000	3,000(?)	2,000(?)
Gabon	200	----	40(?)
Zaire	5(?)	30(?)	10(?)
Upper Volta	----	25(?)	-----
Egypt	1(?)	1	-----
Morocco	1(?)	----	-----
Ghana	1	60(?)	-----
Africa, total	3,208	3,115	2,050(?)
Europe, except USSR.	2(?)	1(?)	10(?)
Australia and Oceania.	100	50(?)	50(?)
USSR Europe and Asia).	3,000	3,000(?)	3,000(?)
Asia:			
India	35	65	50(?)
China	30(?)	50(?)	100(?)
Rest of Asia, except USSR.	5(?)	----	100(?)
Asia (excluding USSR), total.	70	115	250(?)
South America:			
Brazil	100	50	150(?)
Bolivia	2(?)	10(?)	50(?)
Chile	1	----	10(?)
South America, total.	103	60	210(?)
Sea floor nodules	----	200+(?)	5,000+(?)
Rounded total	~6,500	~7,700	~10,000

[1] Identified deposits from which minerals can be extracted profitably with existing technology and under present economic conditions.
[2] Specific, identified mineral deposits whose contained minerals are not profitably recoverable with existing technology and economic conditions.
[3] Undiscovered mineral deposits, whether of recoverable or subeconomic grade, that are geologically predictable as existing in known districts.

picture; firm data are available for few countries, and the figures presented are personal estimates based on evaluation of many sources, published and unpublished. Queried figures are particularly weak and could be wrong by an order of magnitude. Grade of most resources and of ore ranges from 25 to 50 percent manganese.

RESERVES

Reserves are in bodies or districts being mined today. This category includes proved, indicated, and inferred reserves.

CONDITIONAL RESOURCES

Examples of conditional resources are the enormous deposits of manganiferous material deep in the Kalahari basin in South Africa that have been cut by a few deep drill holes. Very large easily accessible deposits are also available there, and accordingly exploitation of the deep beds in the foreseeable future is unlikely. Similarly, the sedimentary manganese carbonate deposits, ranging from 20 to 36

percent Mn, underlying the supergene oxide ores in Ghana, Brazil, and elsewhere are considered as conditional resources. Figures on the size of such bodies are very gross estimates indeed, for none have been explored to depth. Low-grade bodies of manganiferous rocks such as those at Artillery Peak, Ariz., and Aroostook County, Maine, are here included, although they probably will never be used. Also included are the Tambao deposits in Upper Volta, constituting 9 million tons of 50 percent Mn oxide ore plus possibly a greater amount of high-grade manganese carbonate, now without transportation facilities.

HYPOTHETICAL RESOURCES

Included as hypothetical resources are some deposits about which too little is known to include them as identified resources, such as some reported in eastern Bolivia and western Brazil; that such deposits exist is known, but details of size and grade are not accurate enough to include the resource as identified. Similarly, a large area of the southern Ukraine is underlain by manganese deposits like those mined at Nikopol; their presence is said to be indicated by widely scattered drilling, but the possible extent and grade of the whole resource are unknown, and given the enormous known reserve, there is no incentive to establish those facts. Clearly, estimates of such resources can be scarcely more than informed guesses—and not very well informed at that.

The assumptions on which these estimates are based are: (1) sedimentary manganese deposits laid down in a shelf or platform environment may be very extensive, and (2) the possible extent may be judged from the continuity of the geologic environment as witnessed by the associated rocks, even though the manganiferous layer(s) are buried beneath younger rocks. Thus the Molango manganiferous zone is known for some 80 kilometers along strike, although it is below present ore grade for most of that distance. Who can say what might be revealed by exploration back from the outcrop, which is a fortuitous sample of a much more extensive manganiferous zone.

Sedimentary deposits in small tectonic basins, such as some of the Moroccan deposits, cannot be thus extrapolated, nor can the spotty and relatively small hypogene or volcanogene deposits. Similarly, although small deposits of manganese oxide formed by the weathering of manganiferous dolomite or limestone, such as those along the west foot of the Blue Ridge in the Appalachians, remain to be discovered, what will be the cost and the expectable economic return? Such small deposits are not here included. Some districts with residual ore of this type, such as the Postmasburg district in South Africa, have produced millions of tons although known reserves probably never exceeded half a million tons and are here included on the basis of past productivity.

The sea-floor nodules, of course, will represent a great resource of manganese and some other metals when problems of extraction, metallurgical treatment, and legal status have been solved. The true extent of this resource is not yet even approximatly known, but exploration is continuing, and the resource may well eventually reach billions to tens of billions of minable tons. Resource data on nodules given in table 76 are subject to gross modification.

Table 77 gives details of resources and grade of known significant deposits of manganiferous rock that have been considered as potential sources of manganese in the United States. These deposits are included in the identified rsources shown in table 76.

TABLE 77.—*Major identified manganese resources[1] of the United States*

[In millions of long tons. Data slightly modified from Pavlides, (in Hewett and others, 1956, p. 214)]

District	Raw material	Average grade (percent Mn)	Contained Mn
Cuyuna Range, Minn	450	5	22.5
Aroostook County, Maine	280	9	25.2
Chamberlain, S. Dak	69	15.5	10.7
Artillery Peak, Ariz	156	4	6.2
Pioche, Nev	3	10	0.3
Leadville, Colo	3	15	0.5
Total	961	6.8	65.4

[1] Specific, identified mineral deposits that may or may not be evaluated as to extent and grade, and whose contained minerals may or may not be profitably recoverable with existing technology and economic conditions.

Brooks (1966, p. 70–92) ably discussed the technical and economic problems involved in developing these domestic deposits; to the authors' knowledge, no breakthroughs have been made in the metallurgical problems since Brooks' analysis was made. Because capacity of the high-grade ore producers in Brazil, Gabon, South Africa, and Australia was being greatly increased in 1971–72, it is doubtful that the world price of manganese in constant dollars will rise significantly in the near future; the price is lower now in constant dollars than for many years. Accordingly, there is now little stimulus to search for and develop the hypothetical resources here discussed or the speculative resources discussed below.

SPECULATIVE RESOURCES

Speculative resources are impossible to quantify. Manganese deposits of usable mineralogy, size, and grade are too sporadically distributed to permit

sound generalizations as to how much might be present in given areas or volumes of rock. Perhaps this section should be entitled "Guidelines for future prospecting" rather than "Speculative resources."

Presumably, future prospecting will be for medium- to large-scale deposits; when compared with potential reward, the expense of looking for small deposits is prohibitive. In terms of national security, only those deposits that can make a significant contribution to requirements are worth considering; the long lead time in developing significant production emphasizes the need for an adequate stockpile.

For Jurassic and younger deposits, the few volcanogene deposits of economically interesting size and grade are all near the leading edge of the moving tectonic plates, and therefore this type of deposit should be sought in that environment. The large higher grade sedimentary deposits in this age range, however, are all either on the trailing edge of the continental plates or on intracontinental platforms. We cannot yet make similar informed generalizations about pre-Jurassic sedimentary deposits, for the former configurations of the tectonic plates have not been deciphered. Many of the older sedimentary oxide deposits were clearly formed in a platform environment.

In the United States, the largest concentration of manganese is in the carbonate nodules and the enclosing manganiferous rocks of the Cretaceous Pierre Shale in South Dakota. (The resource estimate in table 77 is based on rock with less than ½:1 stripping ratio; the manganiferous beds are very much more extensive. This resource is essentially unworkable at present because of mining, ore dressing, and metallurgical problems; development would perforce hasten silting of important reservoirs.) The source of this enormous quantity of manganese is still unknown. Precambrian iron-formation is in many localities accompanied by or closely associated in time and in space with concentrations of manganese. Some of the iron-formations in the Lake Superior region, notably the Cuyuna range, are highly manganiferous. Although most bedrock in central and western Minnesota is now hidden by Pleistocene glacial deposits, it is known that underlying rocks cause magnetic anomalies and also that a long erosional interval with semitropical or tropical climate took place there during Cretaceous time. The authors think that the manganese in the Pierre Shale may have been derived by intensive chemical weathering, during the Cretaceous Period, of now-buried manganiferous iron-formations or manganese deposits in central or western Minnesota or contiguous areas to the south. The Cretaceous weathering episode may also have created manganese oxide concentrations at that weathering surface. It is of course possible that Pleistocene glaciation may have scoured away such supposed surficial concentrations, which in unglaciated terrane occur on topographic highs.

It is also possible that Precambrian sedimentary deposits of manganese carbonate such as those that gave rise to secondary oxide deposits in Africa, Asia, and South America were present in eugeosynclinal rocks of the Precambrian shields of North America; such deposits are now known in several other Precambrian shields. The characteristically high graphite content of the wallrocks of such deposits might be utilized in geophysical prospecting if cover were not too thick.

Finding of the so-far unique Molango deposit in Mexico raises question as to whether a similar deposit might be present in miogeosynclinal environments in the United States. The gray manganiferous rock at Molango looks like most somewhat-organic limestones and could easily be overlooked; it was discovered during development of small bodies of secondary manganese oxide formed from it by weathering. Most analyses of limestone made in the United States do not determine the manganese content of the rock, and our knowledge of the manganese distribution in limestone in the country is spotty and incomplete. Several carbonate formations in the United States are known to be slightly manganiferous, notably the Shady Dolomite in the Eastern Appalachians. This formation has never been systematically sampled, mainly because it crops out poorly and is in many places covered by debris from other formations. By careful sampling, patterns of manganese distribution in this or other manganiferous carbonate formations might be found, and another Molango might be located. A careful regional study of the Molango area to discover the controls of manganese deposition there would be helpful.

An area of the North American continent that might carry a significant deposit of high-grade manganese oxide is the part of California and northwestern Mexico where the Pacific Rise intersects the continent at the head of the Gulf of California. In Pliocene time the Lucifer manganese deposit (and also the adjacent Boleo copper deposit) in Mexico formed in a basin, probably closed, beside or on this rift zone. The Colorado River has dumped enormous quantities of more recent sediment on this part of the continent, and wells to tap thermal fluids in these sediments in the Salton Sea area and areas to the south in Mexico have brought to the surface steam and water at high temperature and pressure highly charged with mineral salts, including manganese;

the metal content of the steam and water is much higher in California than in Mexico. The source of these metals, which is still unknown, might be the sediments themselves, or underlying rocks, or magmatic bodies at depth. A careful study of the distribution of manganese in the fluids and the direction of their movement might lead to prospecting guides. Such a hypothetical deposit would, of course be very expensive to find and more so to develop, as it would involve underground mining in difficult conditions.

On other continents, the most logical and promising areas are those in which Precambrian eugeosynclinal rocks have been exposed to one or more cycles of erosion and where remnants of ancient erosion surfaces are still preserved. All the significant secondary manganese oxide deposits that formed by weathering of primary sedimentary manganese carbonate deposits are in erosional remnants of such ancient surfaces. In west and central Africa, rocks of Birrimian age are the most favorable and are widely distributed in the western and central parts of the continent. In equatorial Africa, the Francevillian rocks are also favorable. It would be surprising if all the significant deposits have already been found.

In South America the rain forest of the Amazon region to the north and south of the central zone of Paleozoic and younger rocks is possibly the most favorable area; the eugeosynclinal Precambrian rocks in the middle and headwater areas of the north-flowing tributaries are also very favorable. Many occurrences of manganese ores have been located in these areas; probably, commercial deposits will be found, there too on remnants of ancient erosional surfaces. The recent discovery of very extensive areas of oxide-facies iron-formation south of the Amazon increases the possibility of discovery of manganese or manganiferous iron ore associated with these rocks.

In western Brazil and eastern Bolivia at about 20° south latitude, the large known reserves of bedded manganese oxide ore associated with lower Paleozoic oxide-facies iron-formation might be radically increased by more detailed subsurface exploration, not necessarily in the places now known to contain manganese. Here the nearshore facies of the Jacadigo Series is perhaps the prime target for exploration. The known manganese beds are lenticular, although individual lenses may be several square kilometers in extent, and concealed lenses or lenses cropping out obscurely may be of very significant size.

In India the major manganese deposits are metamorphosed primary oxide sediments in lenses of considerable extent. They have not been explored by drilling, and deep drilling probaby will reveal a considerable tonnage of high-grade ore. The economic viability of the deep ore will depend on increased world prices, as such ore will be expensive to extract. India is a manganese-rich province, with deposits of different kinds, largely of sedimentary origin. It would be surprising if further discoveries were not made.

PROSPECTING TECHNIQUES

Prospecting for manganese deposits has been carried on by the classical method of looking for surface indications of manganese oxide. This approach is very usable in areas of outcrop and residual soil because manganese oxide is relatively immobile under most surface and near-surface conditions and because manganese carbonate oxidizes readily to manganese oxide under near-surface conditions.

The high but variable background content of manganese in all rocks, soils, waters, and plants makes geochemical methods difficult, if not unusable. Use of other elements as pathfinders to manganese deposits is hazardous, mainly because most large sedimentary deposits are free of trace elements suitable for this use. Plants may be useful in future manganese exploration. Presence of certain plants, at least locally in the Eastern United States and the Katanga, is indicative of a manganese-rich environment (Cannon, 1971, p. 245).

The common association of graphite and organic carbon with sedimentary manganese carbonate deposits would cause anomalous electrical reactions; therefore induced polarization (IP) and other electrical geophysical methods should be able to detect the carbonaceous wallrocks where these have not been too highly altered. In tropical zones, however, the carbonaceous material is normally oxidized to some depth, so the electrical methods would be applicable only in areas of slight surface alteration.

Once signs of a manganese deposit are located visually, then drilling, test pitting, and exploration of the deposit by adits or shafts are essential to establish the size and grade, for the surficial expression of a deposit may be deceptively large and high grade.

PROBLEMS FOR RESEARCH

GENERAL PROBLEMS

1. The most important problem involved in manganese supply for the United States today is the continuing maintenance of an adequate stockpile of ferromanganese alloys or high-grade manganese ore so that this country will never again be subject to stringent and industrially crippling shortages caused

by interruption, either political or military, of the supply of this essential raw material, all of which is now imported.

2. From the viewpoint of raw-materials supply, the most promising development would be the successful winning of nodules from the sea floor and extraction of the contained metals. This would insure not only a greatly increased resource of manganese but also a significant increment in the supply of nickel, cobalt, and copper—also metals for which the United States is dependent on imports. Large investments are needed to bridge the gap between promising research and pilot-plant operations and industrial-scale application, but the legal status of deep-sea mining must be resolved before large-scale private investment can be secure.

3. Should a decision be reached to attempt to make this country more self-sufficient in manganese supply from conventional sources, greatly expanded metallurgical research would be necessary to tap known submarginal identified resources as well as geological research to locate the hypothetical and speculative resources already discussed.

4. Continuing research into the geological habitat of manganese, causes of concentration into large economic deposits, and the geochemistry of the element can only make the search for conventional and nonconventional sources more fruitful and increase the supply available to our industry and civilization. Because most of the large-scale concentrations and all of the high-grade concentrations of economic size are outside the United States, much of the needed research must be carried out overseas. Judging from past successes and their impact on the supply situation during the last two decades, investment in such research is sound. Specifically, thorough subsurface investigations of at least one of the large carbonate sedimentary bodies, such as Nsuta, Ghana, or Serra do Navio, Brazil, should be undertaken to establish the geological habits and expectable reserves of this type of manganese ore. Such a study probably would have to be subsidized; at present there is little economic justification for a company to undertake research of this type independently because of the abundance of high-grade oxide ores in the world. Results must be published.

NEEDS FOR NEW PROSPECTING TECHNIQUES

Because manganese oxide is very resistant to weathering and usually crops out or is found as concretionary or detrital pebbles or boulders in residual soils overlying significant bodies, prospecting in areas of residual soils is relatively simple. In areas of transported soils or debris and in areas of glacial moraine, loess, or other transported surficial material, or under unconformities, there may be no surface sign of underlying bodies. Geochemical prospecting is much handicapped by the widespread presence of manganese in the earth's crust and the ease with which it is precipitated from solutions under near-surface conditions; positive anomalies are, accordingly, much more common than ore deposits and, by themselves, are relatively meaningless.

Except for a rare magnetic mineral, manganese oxide deposits have no particularly distinguishing geophysical characteristics that would selectively locate concentrations. Manganese minerals have relatively high specific gravity, but many near-surface secondary deposits have so many voids that gravimetric techniques would have only moderate chance of success, although in certain environments the technique has been successfully used (Rowston, 1965). Carbonate-facies sedimentary manganese deposits are in most places closely associated with a high free-carbon content in the wallrocks, and this can be detected under slight or moderate cover by certain electrical methods of prospecting. Unfortunately, many carbonaceous rocks are not associated with manganese deposits, and unless positive indication of the presence of manganese at depth is available, the method is nondiagnostic. In drift-covered areas a combination of geochemical prospecting followed by geophysical investigation in the neighborhood of major anomalies might help locate large bodies of manganese carbonate, but to the authors' knowledge this dual approach has not been attempted and may not be practical. Large manganese carbonate sedimentary bodies are known in many tropical shield areas and may be present but undiscovered in shield areas in northern latitudes. These bodies have hitherto not been exploration targets for economic reasons; the oxide is the preferred ore.

In South Africa, Australia, and the Eastern United States, certain plants have been shown to concentrate manganese in their leaves and (or) twigs. To the authors' knowledge, no extensive research has been done on the general applicability of biogeochemical prospecting to manganese-ore finding; and therefore this is a promising avenue for future systematic research, to determine whether variation in manganese content of plants is a function of generic type, climate, or soil environment.

A better understanding of the exact sedimentary conditions and environment causing large-scale deposition of relative pure manganese minerals in the specific spots in which they are found seems prerequisite to evolving new prospecting techniques.

The general principles are to a large extent known; the reasons why deposits are where they are have not yet been pinpointed and need much closer study and research.

TECHNOLOGICAL PROBLEMS

Manganese carbonate when intimately intermixed with calcite or dolomite or other similar contaminants is difficult to concentrate; similarly, much manganese oxide ore is so intimately mixed with iron minerals or calcite that the constituents cannot be economically separated by known means. Manganese minerals such as cryptomelane, kutnahorite, and braunite inherently contain other elements that cannot be mechanically separated. However, by calcining to drive off carbon dioxide, ores containing much carbonate may be radically upgraded, and ores containing potassium, aluminum, or iron in deleterious amounts can be made usable by mixing with other ores containing less of these elements. Certain elements, such as phosphorus, arsenic, and potassium, are highly deleterious when they occur in amounts above defined limits.

The manganese nodules on the ocean floor contain important quantities of copper, cobalt, and nickel, which must be recovered to make nodule mining economic. Several hydrometallurgical processes have been tried, and one company claims to have solved the problem on an economic basis in pilot-plant studies. Should this be correct, the techniques might be adaptable to recovery of manganese from some of the low-grade resources on land.

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UNITED STATES MINERAL RESOURCES

MERCURY

By E. H. Bailey, A. L. Clark, and R. M. Smith

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ABSTRACT OF CONCLUSIONS

Mercury has several thousand uses, for many of which no substitution is practical or desirable. The annual world production is nearly 300,000 flasks (76 lb each), and the U.S. production in recent years has been less than one-tenth of this amount. In contrast, the United States, to supply its industrial base, has required about one-third of the world production.

In the past few years in the United States, concern over mercury poisoning and pollution has led to legal restrictions, reduced consumption, drastic drop in the price of mercury, and closing of most mercury mines. The geologic outlook for new domestic discoveries of ores rich enough to be competitive in the world market is poor, although there is some possibility in the less explored parts of southwest Alaska. Correlation of occurrences with elements of the "new global tectonic" framework suggests that areas of the Southwest Pacific will be found to contain undiscovered deposits.

Additional domestic research is needed to determine the quantity and mode of occurrence of mercury in the lithosphere, how mercury migrates under geologic processes, how mercury is converted to the highly toxic organic compounds, what are tolerance levels, and how to eliminate or inactivate mercury in already polluted areas. Other research directed toward recovery of mercury from mine and plant wastes would benefit the environment and add to the supply needed by the United States.

INTRODUCTION

Mercury is the only metallic element that at ordinary temperatures is a fluid, which together with its silvery color has led to its being commonly called quicksilver. It has many uses, most of which are for technologically advanced applications, and therefore it is in greatest demand in the most industrialized countries. The United States years ago produced more than enough mercury to supply its needs, but now it consumes one-third of the world production while producing less than one-tenth of the world supply.[1] Much of the U.S. requirement is met by imports, but the total dollar value of the U.S. mercury consumption is relatively small, amounting to $40 million in 1969 and only $15

[1] All statistical data regarding production and consumption for the period since 1932 are from records compiled by the U. S. Bureau of Mines.

million in 1971. When this report was prepared in mid-1972, all major mercury mines in the United States had drastically curtailed or ceased production because of the low price of mercury brought about by concern over mercury pollution.

USES

In addition to being fluid at normal temperatures, mercury possesses a unique combination of properties, such as high surface tension, linear thermal expansion, good electrical conductivity, high density, ability to alloy readily, and tendency to form very toxic compounds. These properties make mercury useful in a great variety of processes and products. Some uses, such as in thermometers or mercury switches, require minute amounts in each apparatus, but others, such as in chlorine-caustic soda plants, require several tons. Amounts and trends by categories are shown in table 78. Note that the two largest uses, electrical apparatus (mostly batteries) and catalysts (chlorine manufacture), together have accounted for about half the U.S. consumption in recent years, and uses dependent on the toxicity of mercury compounds have amounted to another quarter of the consumption. For a detailed review of uses and projected trends for the United States, see reports by the National Research Council (1969) and by Greenspoon (1970).

Metallic mercury of 99.9-percent purity is generally recovered by a distillation process at the mine site, and it is bottled and marketed directly in standard steel flasks containing 76 pounds (about 2.5 liters or 2.7 quarts) of the liquid metal. For some uses, it is redistilled to achieve greater purity and redistributed in glass, plastic, or earthenware bottles containing from 4 ounces to 10 pounds. Mercurial compounds are nowhere made at the mine but are manufactured from refined mercury metal.

TABLE 78.—*Uses and consumption of mercury in the United States*

[Thousands of flasks]

	1942	1951	1970	1971
Agriculture (germicides, fungicides, algaecides)	1.5	7.7	1.8	[1]1.5
Amalgamation (major use before 1900)	.2	.2	.2	0
Catalysts:				
Chlorine-caustic soda (started 1937)	.5	1.5	15.0	12.3
Plastics, resins, acetic acid, other chemicals	3.3	2.6	2.2	1.1
Dental preparations	2.1	1.6	2.3	2.4
Electrical apparatus (mostly batteries)	5.5	13.2	16.0	16.9
Felt manufacture (none since 1943)	.2	0	0	0
Instruments, industrial, control	6.6	10.4	4.8	4
Laboratory, general	.8	.5	1.8	.18
Munitions, blasting caps (none since 1956)	7.8	.6	0	0
Paint, antifouling (mostly ship bottoms)	1.2	2.5	.2	.4
Paint, mildew proofing	0	0	10.1	8.2
Paper and pulp manufacture (slimicide)	0	0	.2	.002
Pharmaceuticals	8.1	2.8	.7	.7
Vermilion (none since 1944)	.2	0	0	0
Other, concealed, unknown	[2]12.2	13.3	[2]6.3	2.3
Total	49.7	66.8	61.5	62.6

[1] Includes fungicides and bactericides for industrial use.
[2] Includes installation and expansion of chlorine-caustic soda plants.

Substitutes for mercury have been found in many formerly important mercury uses, and very little mercury is now used for amalgamation (largest use in 1870's), antisyphilitics (largest use in 1917), munitions, detonators (fulminate), felt manufacture, pattern making, paper manufacture, vermilion, fireworks, and cosmetics. In some other major uses, substitutes could be used but would result in sacrificing quality of the product or economy of manufacture, or both. For example, in the manufacture of chlorine-caustic soda, a diaphragm cell can be used instead of the mercury electrolytic cell, but it yields a product of lower purity at a higher cost, which ultimately affects the price of nylon, rayon, petroleum products, aluminum, detergents, and many other consumer items. However, for many uses, such as batteries, mercury lamps, wall switches, thermostats, barometers, manometers, thermometers, pressure gages, and laboratory uses, substitution is impractical and undesirable. For agricultural uses and paint, substitution may in the future be practical as nonmercurial germicides and fungicides having selective toxicity are discovered.

SIZE AND IMPORTANCE OF THE INDUSTRY

World production of mercury reached an all-time high in 1969 of 290,000 flasks, valued at about $159 million. U.S. mercury production in the same year was 29,640 flasks, valued at about $15 million, or 0.02 percent of the $7.2 billion of national income generated by mining. The importance of the mercury industry, however, outweighs its relative size. About 300 U.S. companies use primary mercury, and another 400 that use redistilled mercury account for about 20 percent of the total U.S. consumption. Almost everyone safely uses a little mercury every day, and without it we would be forced to use inferior products made at increased cost. It is classified by the U.S. Government as a strategic commodity, essential to the economy. Financial assistance in exploration for new mercury deposits is provided by the Government through the U.S. Geological Survey, Office of Minerals Exploration. Of the 36 eligible commodities, mercury is one of nine eligible for assistance of 75 percent of the allowable costs of exploration, as compared with 50 percent for the others.

EXPLOITATION

MINING

By most mining standards, mercury mines are all small. The largest probably is the New Almaden mine in California, where about 30 miles of horizontal underground workings were driven for ex-

ploration or development over a hundred-year period. To avoid high labor costs, in the past 30 years a diligent search has been made in the United States for large low-grade surficial deposits, but the only really major deposit that has been mined by open-pit methods is that of the Sulphur Bank mine also in California, which was discovered 100 years ago.

Mining and recovery costs at mercury mines vary so widely that averages seriously oversimplify the picture. At open-pit mines, ore containing 2 pounds of mercury per ton ($5 per ton in 1963) has been successfully treated, but concurrently some underground mines have lost money on ore containing 10 pounds per ton. In 1970 the Quinn River mine (formerly Cordero) in Nevada closed when the price fell below $425 a flask, and in 1972 the major New Idria mine in California was closed when the price fell below $160 a flask. For comparative purposes, the best guides to costs are price-production curves (fig. 46). At any given price, some mines lose money, others break even, and only a few make a profit. Average costs generally approach average prices within a few percent.

PRODUCTION

Total world production during this century has ranged from 65,000 flasks in 1933 to 290,000 flasks in 1969 (fig. 46). Probably nearly 1,000 mines in the world have each produced more than 100 flasks of mercury, but three-fourths of the world production has come from only six mines or districts.

Domestic primary production fluctuates wildly in response to short-term variations of a few hundred percent in price. The peak U.S. production, almost 80,000 flasks, was in 1877. Since then, the domestic industry has undergone a half dozen cycles of stimulated production, in response to higher prices, followed by collapse, on the heels of lower prices. By 1943, under war-time conditions, production had risen from the less than 10,000 flasks produced 10 years before to almost 52,000 flasks. By 1950, production had again dropped, to a new low of 5,000 flasks. After another cycle, production rose in 1969 to 29,000 flasks in response to all-time high prices. Our production through the years has come from over 300 mines in 11 States (table 79); however, just as is true for world production, three-fourths of the domestic output has come from six mines, all of which are in California.

The U.S. proportion of world production, with generally rising demand, has declined from more than 60 percent in 1877 to less than 3 percent in 1950 and 6 percent in 1971. The proportion of U.S. consumption coming from domestic mines reached a low of 9 percent in 1950 but rose to 33 percent in 1971. This seeming improvement, however, is the result of temporary curtailment of consumption because of pollution problems and does not reflect increased production.

Secondary production of mercury in the United States, first reported in 1946, has become increasingly important in helping to make up the difference between U.S. requirements and mine production. Most of the mercury reclaimed is from electrolytic cells, mercury boilers, discarded instruments, battery scrap, dental amalgam, and electrolytic, oxide, and acetate sludges. Secondary recovery is made by six processors and four scrap dealers in

TABLE 79.—*Mercury produced in the United States, by States*

[Flasks of 76 lb]

State	First production	1850–1949	1950–59	1960–69	1970	1971
Primary (from mines):						
Alaska	1923	4,650	16,919	14,151	[1]	[2]
Arizona	1908	6,034	819	1,439	----	----
Arkansas	1931	11,404	----	350	[1]	[2]
California	1850	2,623,873	110,793	163,042	18,593	13,233
Idaho	1917	14,731	14,258	7,927	1,038	1,057
Nevada	1903	72,995	46,245	54,422	4,909	1,589
New York	1969	----	----	280	28	[2]
Oregon	1870's	89,284	13,629	4,779	274	[2]
Texas	1899	146,655	1,552	1,885	[1]	[1]
Utah	Early 1880's	3,497	------	------	-----	-----
Washington	1916	6,604	20	34	[1]	----
Total primary		2,978,727	204,235	248,309	27,296	17,627
Annual number of producing mines		1–197	16–147	48–149	79	60
Annual averages of mercury recovered (lb per ton of ore)		735–4.9	9.3–6.4	13.6–4.1	4.8	----
Secondary	1946	11,055	47,430	[3]94,459	[3]8,051	[3]16,666

[1] Alaska, Arkansas, Texas, and Washington, 2,464 flasks in 1970.
[2] Alaska, Arkansas, New York, Oregon, and Texas, 1,748 flasks in 1971.
[3] Includes GSA releases 1963–71.

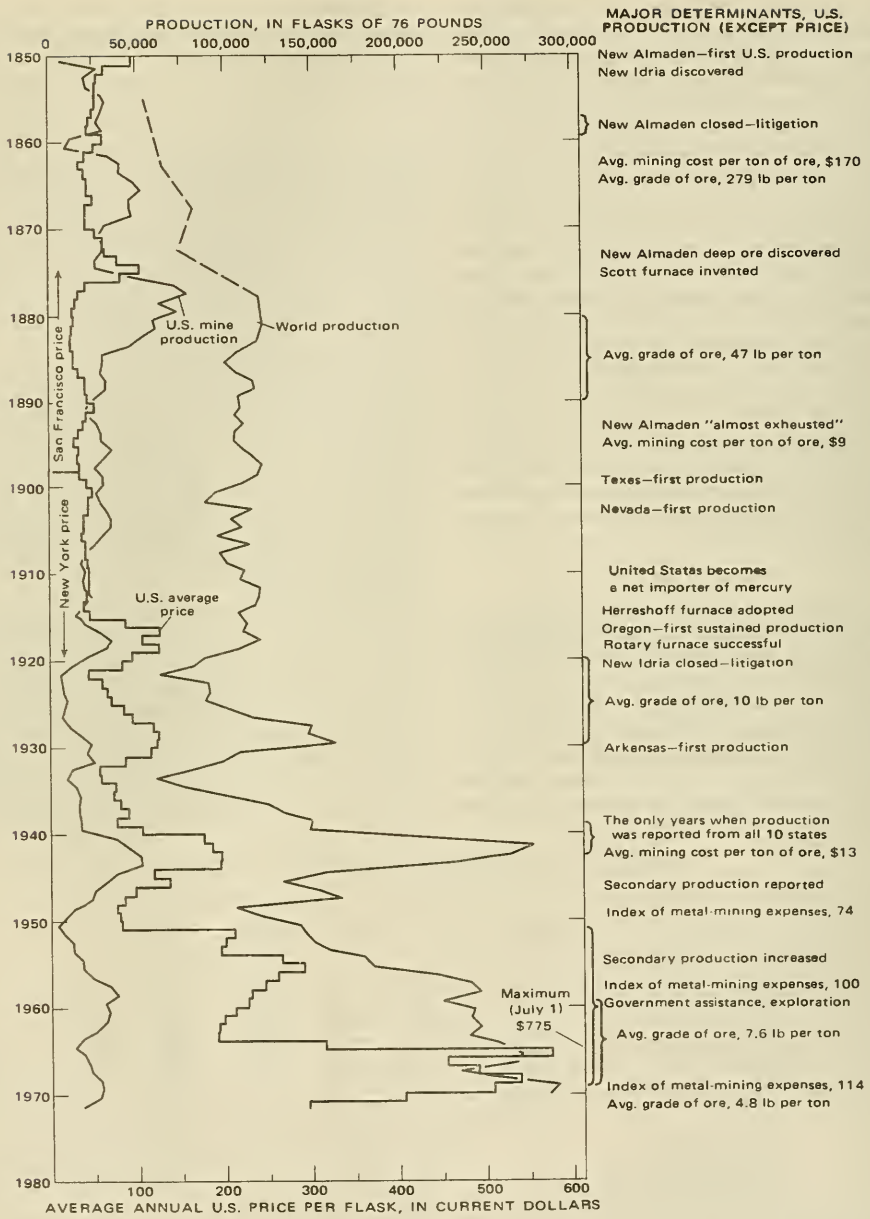

FIGURE 46.—Mercury production and prices, 1850–1971. From U.S. Bureau of Mines Minerals Yearbooks.

TABLE 80.—*Mercury supply and demand in the United States*

[Thousands of flasks]

	1860–1949	1950–59	1960–69	1970	1971
Mine production (started 1850)	2,979	204	248	27.3	17.6
Secondary production (started 1946)	----	47	[1]94	[1]8.1	[2]16.7
Imports (started 1868)	----	505	231	21.7	29.7
Total supply	----	756	573	67.1	64.0
Consumption (no record before 1867)	----	516	700	61.6	62.5
Exports (started 1864)	----	7	20	4.7	[2]7.2
Total demand	----	622	720	66.2	69.7
Surplus or deficit	----	234	−147	−9.1	4.3

[1] Includes GSA sales of 72,366 flasks in 1966–69 and 701 flasks in 1970.
[2] Includes GSA exports of 5,700 flasks to AID.

the United States. Official figures compiled by the U.S. Bureau of Mines (table 80) are somewhat confusing because sales and releases of primary mercury from the Government stockpile by the General Services Administration are included under secondary recovery. In 1964 these releases included 7,000 flasks to other Government agencies and 10,000 flasks to the Department of Health, Education, and Welfare for donation to more than 3,000 hospitals and schools. In 1971 there were no GSA sales, but 5,700 flasks were transferred to the Agency for International Development for shipment to India.

PRICES AND TARIFFS

The U.S. price has averaged as low as $28.56 a flask, in 1883, and as high as $570.75, in 1965; but it reached an intraweekly all-time high of $775 on July 1, 1965 (fig. 46). When this report was prepared in mid-1972, the price was only $165 a flask.

The world (London) price is generally lower than the New York price by roughly the amount of the U.S. tariff, but monthly averages range from about $80 lower to $35 higher.

There are no special federal taxes on mercury production, although some States impose a tax on the proceeds of all mines. An import tariff of $19 per flask in effect since 1922 was reduced to $15.20 on January 1, 1969, to $12.92 on January 1, 1970, and to $11.40 on January 1, 1971. A depletion allowance for new domestic discoveries of 15 percent since 1932 was increased to 23 percent under the Internal Revenue Code of 1954 and has continued through 1971. The allowance is limited to 50 percent of net income.

OUTLOOK

Until just before World War I the United States produced more mercury than it consumed (fig. 47). Ever since, it has relied to greater or lesser degree on imports to supplement domestic mine production, except during the World War II period, when, with high prices and some Government support, domestic mines virtually filled the U.S. requirements. It has been generally felt that if the price of mercury were high enough, United States mining could supply all domestic needs, although production response to the increased price would lag 2–4 years behind the price increase. In 1965 the price rose to unprecedented levels, but the mine production response peaked in 1969 at about 29,000 flasks, which was only one-third of the domestic consumption. It has become obvious that, as predicted (Bailey and Smith, 1964), the U.S. supply of known, or even suspected, mercury ore of grade competitive on the world market is entirely inadequate to meet domestic needs. The current outlook for discovery of large high-grade deposits in the conterminous United States is unpromising, but in less explored southwestern Alaska major discoveries may be possible.

As a result of concern about pollution, the demand for mercury in the United States has diminished considerably, but concurrently the price has fallen so low that domestic mine production will not supply even the reduced demand.

Until higher grade foreign deposits are depleted—which, it is estimated, will not be for at least 25 more years at Almadén, Spain—the United States will remain a net importer of mercury, owing to the low grade of ore available and the relatively high cost of mining it. However, the maintenance of some domestic industry, even if for no other reason than to provide a bargaining base, is highly desirable.

GEOLOGIC ENVIRONMENT

BASIC GEOCHEMISTRY

A little mercury occurs in almost all natural substances—rocks, soils, water, air, and both animal and vegetable organisms—but analytical techniques sufficiently sensitive to measure the minute amounts involved have been perfected only recently. Al-

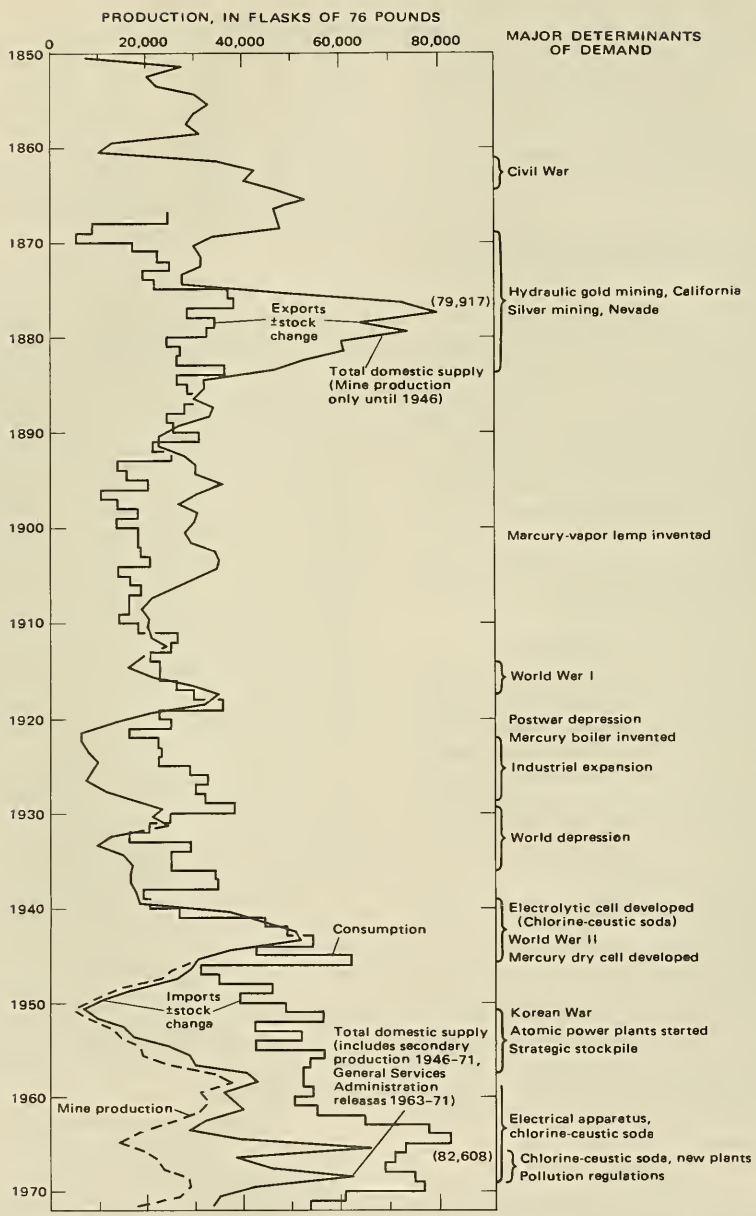

FIGURE 47.—Demand and domestic supply of mercury in the United States, 1850–1971. From U.S. Bureau of Mines Minerals Yearbooks.

though there is much variation, typical amounts can be given (table 81).

The average mercury content of continental rocks has been calculated at about 80 ppb (parts per billion) (Taylor, 1964), and a similar figure was calculated for the earth's crust (Saukov, 1946). More recent work (Ehmann and Lovering, 1967) suggests that these values may be a little too large, but they are certainly the right order of magnitude. In contrast, the content of a minable mercury ore deposit must be at least 2 pounds to the ton, or 1,000,000 ppb (0.1 percent), representing a mercury concentration 10,000 times greater than the usual content of most rocks.

For additional details regarding the occurrence of mercury compounds in nature and their behavior during the weathering cycle, see Tunell (1970).

TABLE 81.—*Mercury content of various natural substances*

[Most data from U.S. Geol. Survey (1970)]

	Parts per billion
Igneous rocks:	
Peridotite, dunite, basalt	5 – 20
Andesite, granite	15 – 100
Sedimentary rocks:	
Sandstone	20 – 75
Shale	100 – 1,000
Limestone	15 – 50
Coal	10 – 1,000
Metamorphic rocks	20 – 200
Soil	10 – 100
Natural fluids:	
Rain water	.2
River water	.1
Ocean water	.03– 1
Petroleum	2,000 –20,000
Air	.01
Organisms:	
Plants	<500
Fish	20 – 200
Mammals	<20

ORE DEPOSITS

All major mercury deposits are mined for their mercury content alone, and all contain the red mercuric sulfide, cinnabar, as the chief ore mineral. Liquid mercury metal and a black mercuric sulfide, metacinnabar, are locally of some economic importance, and in one medium-size deposit a mercury-antimony sulfide, livingstonite, was the main ore mineral. The more than a dozen other known mercury minerals are relatively rare and inconsequential as sources of mercury.

Within the past few years, mercury has been produced as a byproduct at the Gortdrum copper mine in Ireland (1,300 flasks per yr), the Rudnany zinc-copper mine in Czechoslovakia (1,000 flasks per yr), and the Carlin gold mine in Nevada (60 flasks per yr). Cinnabar has been identified at all of these deposits, but other minerals probably also contain small amounts of mercury. The St. Joe Minerals Corp. smelter in Monaca, Pa., also recovers mercury (300 flasks per yr) from zinc concentrates from deposits in New York, but the mercury-bearing mineral is unknown.

Silica and carbonate minerals are the common introduced gangue minerals in mercury deposits, but pyrite and marcasite may be abundant in deposits formed in iron-bearing rocks. Stibnite is rare but is more common than orpiment. Other metals, such as gold, silver, or base metals, are generally present in only trace amounts. An exception, however, is a base-metal assemblage containing mercurian tetrahedrite, from which mercury has been recovered in a few places.

The ore-forming mercury minerals, and introduced gangue minerals, are deposited from hot solutions at temperatures from perhaps 50°C to 200°C, and they thus form relatively low-temperature, epithermal deposits (White, 1967; Tunell, 1970). The deposits are characteristically shallow, and in the United States only half a dozen have been mined at depths greater than 1,000 feet. Even in the major mercury deposits of the world, ores have not been mined more than about 2,000 feet below the surface, although at the largest, the rich Almadén mine in Spain, ore is reported to have been drilled at depths of 3,000 feet. The greatest depth at which cinnabar has been found is reported to be 5,900 feet, in a well drilled for geothermal steam in the Geyser area, Sonoma County, Calif. (G. H. Gaul, written commun., Feb. 22, 1969).

Mercury ore deposits have doubtless been formed throughout geologic time; but owing to their shallowness, those deposited long ago have been either eroded away or covered over so they cannot be seen. Very young deposits, still uneroded and uncovered, constitute the discoverable and minable ore bodies. Because they were deposited in preexisting rocks, almost any kind of rock might be the host, though some varieties have unusually favorable chemical or physical properties. However, the distribution of mercury deposits about the world is restricted because the volcanic and tectonic activity responsible for generating the heated pregnant solutions that deposited the mercury has in recent time taken place only in limited belts (Bailey, 1959). One highly productive belt extends northward along the western part of South and North America, passes through central Alaska, extends southward through Japan, then turns westward across central China and through the southern part of the Soviet Union and Europe. Other shorter and much less productive belts extend from New Zealand up through Papua–

New Guinea and along the Indonesia-Sumatra arc. (See fig. 48). Although the deposits are in belts of volcanic activity, many major ore bodies are remote from any young volcanic rocks.

The six most productive mines or districts, and their approximate production, are:

	Flasks
Almadén, Spain	7,500,000
Idria, Yugoslavia	3,000,000
Monte Amiata, Italy	2,000,000
Santa Barbara, Peru	1,500,000
New Almaden, Calif	1,100,000
New Idria, Calif	600,000

Very brief descriptions of the geology of these most important deposits will serve to show the diversity of occurrence that characterizes mercury deposits.

The famous Almadén mine, which has yielded about one-third of the world production, is in an area of folded and faulted shale, limestone, and quartzite of Ordovician to Devonian age (Mamen, 1971). Igneous rocks are represented in the mine area by narrow diabase dikes; the nearest major intrusive is a granite batholith 25 kilometers away. The ore bodies occur in three parallel vertical quartzite beds that from the surface to a depth of at least 750 meters are extensively replaced by cinnabar and locally impregnated with native mercury. The most productive bed is 30 feet thick, and a central zone about 10 feet thick contains in some places more than 10 percent mercury. The minable strike length is over 1,000 feet on the 17th level. Average grade of ore treated is about 2 percent.

The Idria mine in northwestern Yugoslavia lies in a thick sequence of sedimentary rocks ranging in age from Carboniferous to Eocene and occurring in four superposed thrust sheets (Mlakar, 1964). Most of the ore is formed by cinnabar that has replaced Permian and Triassic dolomite, but some occurs in shale or sandstone. Individual ore bodies are large, many having a plan area of over 20,000 square feet and extending through a vertical interval of 200 feet. Ore has been mined to a depth of 1,300 feet. In recent years, an ingenious solution of a fault problem led to the discovery of a wholly new major ore zone offset 2 miles from that which has been mined for the past 450 years. Because only sparse native mercury occurred in the uppermost thrust plate and rich cinnabar occurred in the plate below, it has been suggested that the ore was formed in Triassic time, before the thrust faulting, and thereafter was protected from erosion by being covered by the overthrust plate. The near-surface native mercury is believed to be the result of postore and postthrust upward migration of vapor from the main ore body. The grade of ore processed ranges from 0.1 to 0.2 percent.

The major mine of the Monte Amiata district, central Italy, is the San Salvatore, which is on the lower slopes of Monte Amiata volcano (Eckel, 1948). The rocks below the lava are much deformed and broken beds of Eocene limestone and shale. Ore bodies of detrital cinnabar occur in curious solution caves in limestone, which are widest just beneath the lava and taper downward to narrow roots several hundred feet below the contact. The ore bodies were formed by rising hot solutions that first deposited cinnabar just below the contact and later dissolved the limestone, releasing the cinnabar to accumulate in the caves. Other, deeper primary ore bodies consist of cinnabar coatings on broken limestone and shale. The grade of ore treated is about 0.4 percent.

The Santa Barbara mine, high in the Andes near Huancavelica, Peru, once rivaled Almadén, Spain, in production but has had only minor production in the past century. Mesozoic limestone, sandstone, and shale are overlain by a great pile of Tertiary volcanic rocks and intruded by volcanic breccia. Tabular ore bodies occurred through a depth range of about 1,000 feet in places where cinnabar filled pore spaces or fractures in sandstone or voids in volcanic breccia. The average grade was about 2 percent, though ore mined in recent years is much leaner.

The New Almaden mine in California (Bailey and Everhart, 1964) is the greatest mercury producer in North America, but most of its yield came prior to World War I. In the mine area, folded and faulted Mesozoic eugeosynclinal sedimentary and volcanic rocks are intruded by serpentine, which in Tertiary time was altered along its margins to silica-carbonate rock. Rich ore occurs where silica-carbonate rock was replaced by cinnabar along steep parallel fractures, and large ore bodies were found from the surface to depths of about 2,000 feet. The grade of all ore recovered through the life of the mine is about 4 percent.

The New Idria mine in central California (Linn, 1968) is the second most productive mercury mine in North America and was a major producer until the spring of 1972. The mine is near the northern margin of a pluglike mass of serpentine that has arched upward and pierced through a thick Cretaceous shale-sandstone sequence. Steeply dipping shale near the serpentine has been rendered brittle through induration, and subsequently shattered. Most ore bodies occur where cinnabar alone fills the fractures or coats their walls, but some cinnabar and

metacinnabar occur in thick carbonate veins. The largest ore shoot in shale was 300 feet long, 25–150 feet wide, and 800 feet high. Ore mined in the early days contained 10 percent cinnabar, but for the past 30 years, mined ore has averaged less than 1 percent.

These deposits have in common cinnabar as the major ore mineral and comparatively shallow depth, but little else. Some are in sedimentary rocks such as limestone, quartzite, or shale, and some are in volcanic breccia or altered serpentine. Some major ore bodies have been formed by replacement, others by open-space filling, and others by both, and some are a result of detrital concentration. The thousand or so smaller deposits not described in this report likewise show a diversity of mineralization, host rocks, rock alteration, and structural localization.

RESOURCES

IDENTIFIED RESOURCES

At most mercury mines, no effort has been made to ascertain the ultimate reserve of the deposit in advance of exploitation, and at few mines is enough ore blocked out for more than 1 year of operation. Major exceptions are at some of the larger foreign deposits, such as Almadén or Idria, but even at these no attempt is made to learn in advance the complete resource. In the Soviet Union, much effort is expended in trying to determine the ultimate reserves before mining, with only indifferent success for mercury deposits, but all reserve figures are closely guarded. Hence, no one knows the total reserves or resources of the major mercury deposits of the world, and only estimates based on production records and familiarity with the geologic habits of the ore can be made. On this basis, we have estimated the resources of known areas by countries or by groups of countries (table 82).

TABLE 82.—*Identified mercury resources of the world* [1]
[Given in thousands of flasks in ore minable at price per flask indicated]

	$400	$1,000
United States	170	490
Canada	200	400
Mexico	300	700
South America	50	300
Spain	2,500	6,000
Italy	750	2,000
Yugoslavia	1,000	2,000
Czechoslovakia	15	30
Africa	30	60
Japan	60	200
Turkey	60	200
Philippines	50	200
U.S.S.R.	1,000	3,000
Communist China	1,000	1,500
Total	7,185	17,080

[1] Identified resources: Specific, identified mineral deposits that may or may not be evaluated as to extent and grade, and whose contained minerals may or may not be profitably recoverable with existing technology and economic conditions.

Estimates by States, made on a similar basis but with greater familiarity with the deposits, are given in table 83.

TABLE 83.—*Identified mercury resources of the United States, by States* [1]
[Given in thousands of flasks in ore minable at price per flask indicated]

	$400	$1,000
Alaska	25	100
Arizona	1	6
Arkansas	---	1
California	100	300
Idaho	10	25
Nevada	20	30
New York	5	5
Oregon	5	10
Texas	4	10
Utah	---	1
Washington	---	2
Total	170	490

[1] Identified resources: Specific, identified mineral deposits that may or may not be evaluated as to extent and grade, and whose contained minerals may or may not be profitably recoverable with existing technology and economic conditions.

A word of caution seems required in the use of these numbers, especially those for the United States. Although these estimates are for ore in known ore-bearing areas, they do not represent known ore. At $400 a flask, even if the ore were minable once it had been found, the cost of finding it might be excessive. Thus, while U.S. mines offer a potential at this price, few will be reopened or explored by other means until the price is higher or is expected to go higher. For other estimates of resources at various prices, see U.S. Bureau of Mines (1965).

SPECULATIVE RESOURCES

Masses of rock containing concentrations of mercury rich enough and large enough to form minable, or even near-minable, ore deposits are exceedingly rare. The surface area underlain by known mercury ore throughout the world probably does not exceed 50 square kilometers, which is about one three-millionth, or 0.00003 percent, of the earth's land area. In considering the mercury potential of the world, or in the search for new mineralized areas, the economic geologist concerns himself with the question of what parts of the remaining 99.99997 percent might be underlain by mercury ore. We expect we are searching for places comparable in size to known ore bodies, which in proportion are even smaller than the proverbial needle in a haystack. Origin and geologic occurrence of known deposits provide the best clues about where to look and the best data for predicting the potential of unexplored areas.

During the past century, geologists noting the global distribution of mercury deposits about the Pacific, with a branch extending westward from

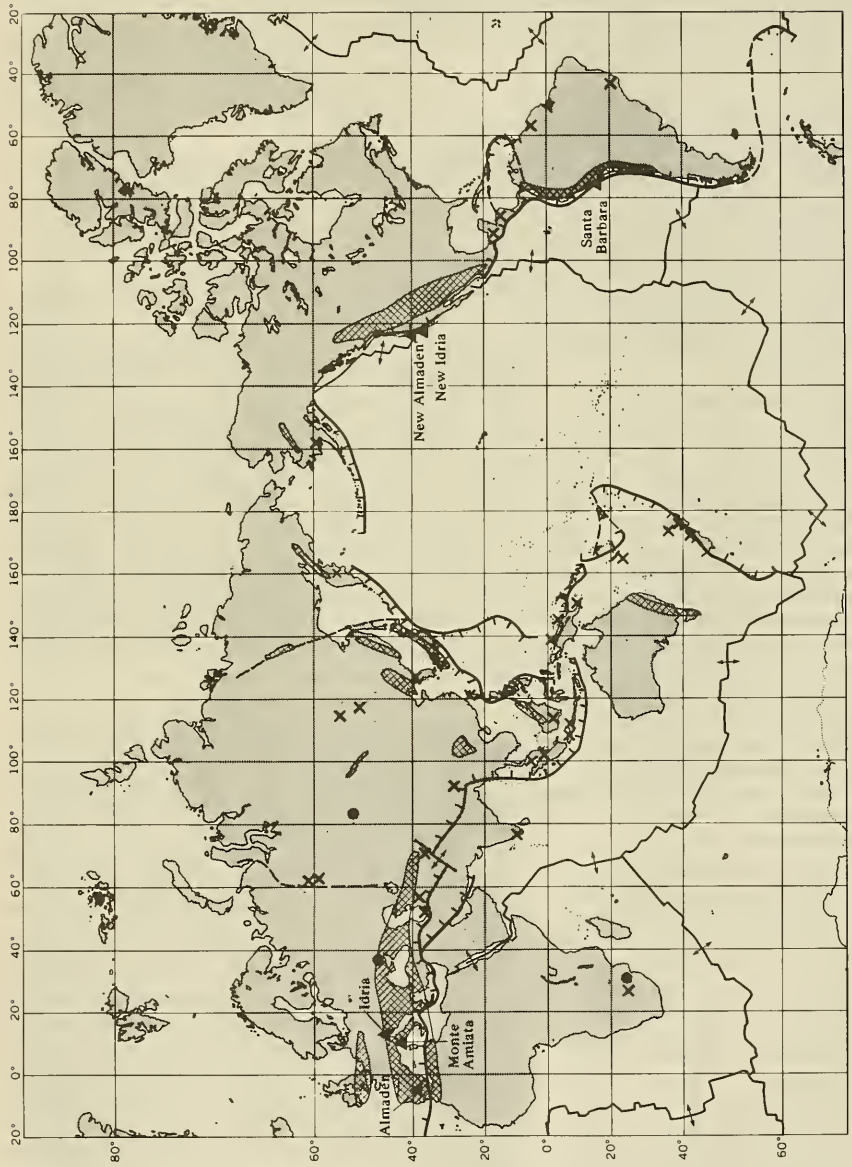

FIGURE 48.—Relation of mercury deposits of the world to post-Jurassic subduction zones.

southern China through southern U.S.S.R. to the Alpine belt of southern Europe (Bailey, 1959), have correlated their distribution with a general Tertiary belt of volcanoes referred to as the "belt of fire." In the past 6 years, geologists have recognized the relation of major tectonism and volcanism to moving crustal plates and have developed the revolutionary "new global tectonics" (Heirtzler and others, 1968; LePichon, 1968). Comparison of the occurrence of mercury deposits with the new global elements (fig. 48) shows that most deposits occur on the continentward side of post-Jurassic subduction zones. Especially, they are localized where oceanic crust and its accompanying trough deposits are swept downward beneath the margins of blocks of continental crust. This suggests that the mercury originally contained in the marginal eugeosynclinal sediments, or perhaps even in oceanic crustal material, has been distilled out of the downward-plunging plate and emplaced at a higher, cooler level along or above the subduction zone. Additional search in the less explored parts of the world lying close to such subduction zones, such as in Indonesia, on Kamchatka, or in the Papua-Fiji belt, should find entirely new mercury districts.

In the main mercury belt of the United States, which trends through the California Coast Ranges and has yielded 85 percent of the U.S. production, global tectonic relations also apply in a striking and significant fashion. As shown in figure 49, virtually all the productive deposits lie close to, and generally just below, the Coast Range thrust, which is a major late Mesozoic subduction zone (Bailey and others, 1970). This major structure provides an unusually fine guide to where to look for more ore, but through the past 100 years, the part of California indicated to be most favorable has been so well explored that the discovery of new mercury deposits of significant size cannot be expected.

The use of principles of global tectonics indicates areas to be explored for new mercury deposits, and new ones will probably be found along the favorable belts. Considering the rate of discovery of the past 100 years, it seems likely that even with better geologic guides and exploration techniques, the amount of mercury discovered in new districts will not equal the amount consumed. Most of the undiscovered resources will come from new ore bodies to be found in districts now being exploited.

PROSPECTING TECHNIQUES

The most widely used, and most successful, prospecting technique has been simple panning of stream sediments or slope debris. Most standard geophysical methods have been tried, but they do not seem to be generally applicable to the search for mercury deposits. In recent years, various geochemical exploration techniques have been used with some success. Stream sediment sampling has been done by Clark and others (1970a, b, c, and 1971), and soil sampling has been widely used. Shacklette (1965) has applied geobotanical methods, and McCarthy, Vaughn, Learned, and Meuschke (1969) have shown that determination of mercury vapor in soil or air over deposits is useful for locating mercury or some base-metal deposits. Recent refinements of methods for measuring trace amounts of mercury have made geochemical methods of prospecting more reliable and useful (Barringer, 1966; Dinnin and Worthing, 1966; Hinkle and others, 1966; Vaughn, 1967; Manning (1970), Plimmer and Klingebiel, 1971; Weissberg, 1971).

PROBLEMS FOR RESEARCH

The immediate problems of mercury supply for the United States are chiefly nongeologic. For many years the domestic mercury-mining industry has had difficulty competing with foreign producers who have such rich ores and cheap labor that they can undersell U.S. producers, thus closing down U.S. mines. Intensive exploration might find a new rich ore body in the United States, but the chances of such a discovery are small. The problems of utilizing our lower grade ores are well known and need no discussion here. However, in the past 5 years a new problem has been introduced—that of the undesirable effects of mercury pollution—and much research is needed to evaluate properly the degree of mercury pollution brought about by industrialization and its effects.

Both mercury liquid and vapor, as well as nearly all compounds of mercury, are toxic; fortunate exceptions are the most common ore minerals, the mercuric sulfides. Mercury poisoning has been recognized for centuries and has been guarded against by both mercury mining and utilizing industries. Recently, it has become a concern, partly because of public awareness regarding general environmental deterioration, and partly because recent improvements in detection and measurement techniques have for the first time allowed accurate determination of low-level mercury contamination. In addition, the increased use of mercurial germicides and the more numerous chlorine-caustic soda plants discharging mercurial waste into lakes and rivers have led to identified cases of mercury poisoning of birds, fishes, and humans (Goldwater, 1971; Wallace and others, 1971).

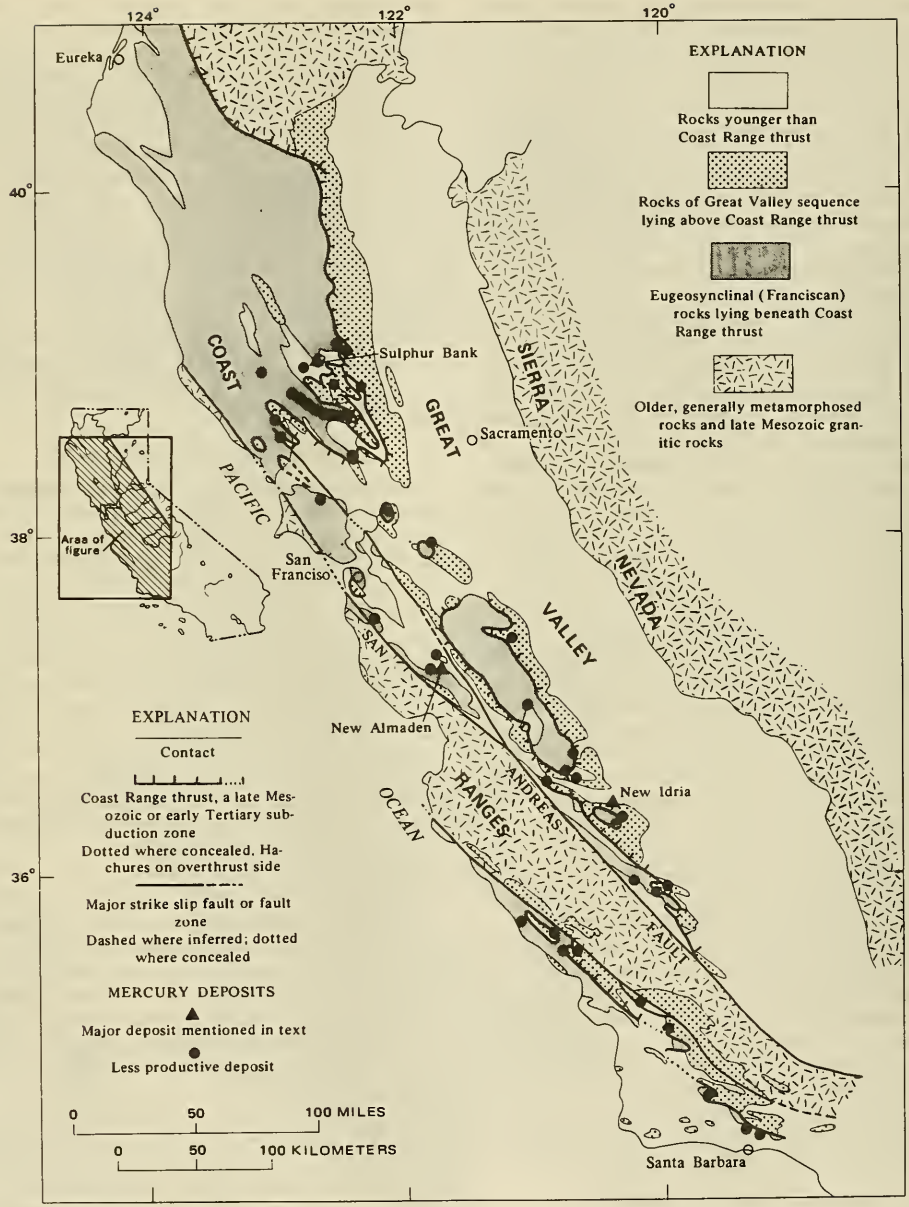

FIGURE 49.—Relation of mercury deposits of California to the Coast Range thrust.

In the early 1950's, in Sweden and Finland, population declines of seed-eating birds were traced to methyl mercury used as seed dressing for the prevention of plant diseases, and similar declines among birds living on fish from waters contaminated by methyl mercury were also found. Sweden banned the use of mercurials in seed dressing in 1966, and the sale of fish from about 40 lakes in 1967. Also, in Iraq (1956), West Pakistan (1961) and Guatemala (1963), humans were poisoned by eating seed grain treated with mercurial fungicides.

In Japan, between 1953 and 1960, 110 people were poisoned by eating fish from Minamata Bay, which was contaminated by methyl mercury in waste water from a plastics plant; subsequently, 52 deaths were reported. Fishing was prohibited, and mercury was eliminated from the discharge. In Niigata, Japan, in 1965, five deaths resulted from 26 cases of mercury poisoning; the people poisoned had been eating fish containing as much as 20 ppm (parts per million) mercury as often as three times a day. The plant to which discharges were traced was closed.

In the United States in 1969, several members of a farm family in Alamagordo, N.Mex., were poisoned by eating pork from hogs that had been fed seed grain treated with a fungicide containing mercury.

In Canada in 1970, walleye pike in Lake St. Clair were found to contain as much as 7 ppm mercury. The mercury was traced to the discharges from two chlor-alkali plants—one at Sarnia, Ontario, and the other in Michigan—and commercial fishing in the lake was prohibited. In the United States in late 1970, food testing revealed 0.18 to 2.4 ppm mercury in swordfish and as much as 1.12 ppm in 138 samples of canned tuna tested. Both were removed from the markets (2⅓ million cans of tuna), but tuna was later declared safe to eat. Subsequently, analyses of seven museum specimens of tuna caught between 1878 and 1909, and of one swordfish caught in 1946, showed mercury in about the same amount (0.13 to 1.27 ppm) as specimens caught in 1971.

By mid-1972, the use of 12 pesticides was prohibited, registration of 48 mercury compounds used for algaecides, slimicides, and commercial laundering was suspended, and use of 750 other compounds was conditionally cancelled. Proposed mercury-emission standards would prohibit the release into the atmosphere of more than 5 pounds per 24-hour period, which would be difficult for a large mercury furnace plant to meet (Federal Register, 1971).

More research is needed to ascertain the quantities of mercury in various environments in the lithosphere, the reaction of mercury minerals in the weathering and transportation cycle, the formation of the easily assimilated toxic organic mercury compounds, the distribution of mercury in the biological food chain, and human tolerance levels.

Other research should be directed toward improved techniques for recovery of mercury not only from ores but especially from industrial wastes. Such research could simultaneously improve the environment and provide some of the mercury needed by our highly industrialized society.

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MICA

By Frank G. Lesure

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ABSTRACT OF CONCLUSIONS

Sheet mica has been an important strategic mineral used in electrical appliances, vacuum tubes, capacitors, and various other electrical and nonelectrical products. The United States has not been self-sufficient in sheet-mica production since before the turn of the 20th century and has imported supplies to meet half to all of its needs, mostly from India, Brazil, and Malagasy Republic. Sheet-mica uses are declining with advancing technology and introduction of substitutes. Although the United States has undiscovered and paramarginal resources of sheet mica, the high cost of the necessary hand labor involved in mining and preparation of sheet mica deters exploration, development, or further mining.

Average United States scrap-mica production is increasing, but reserves and resources are adequate for foreseeable demand. The United States is self sufficient in flake-mica production and is a net exporter of ground mica.

INTRODUCTION

Mica is the general group name for several complex hydrous aluminum silicate minerals. The principal mica minerals are muscovite (white mica), biotite (black mica), and phlogopite (amber mica). All have a perfect basal cleavage and form crystals that can be split into thin sheets having various degrees of transparency, toughness, flexibility, and elasticity. The micas are common minerals in igneous, metamorphic, and some sedimentary rocks. Muscovite is the most important commercial mica in the United States. Phlogopite is generally inferior to muscovite except in uses that require resistance to high temperature: muscovite breaks down at temperatures of more than 500°C, whereas phlogopite is relatively stable up to 1,000°C. Biotite is inferior to muscovite and phlogopite and has little commercial value.

TYPES AND USES OF MICA

Two types of mica are sold: sheet mica, which must be relatively flat, free from most defects, and large enough to be cut into pieces at least 1 square inch; and scrap mica, which is all mica that does not meet sheet-mica specifications and that is generally ground to a powder. Small sheets of untrimmed mica of poorer quality that can be punched or trimmed into disks at least 1 inch in diameter

are classified as punch mica and are included in the general term "sheet mica." Built-up mica made from very thin sheets and reconstituted mica made from scrap can be substituted for larger sheet mica for some uses.

SHEET MICA

Sheet mica is an important dielectric and insulating material used in the manufacture of electronic and electrical equipment, such as electronic vacuum tubes for radio and television, capacitors, motors, transformers, generators, and electrical appliances. Nonelectric uses include shields for high-temperature steam-gage glasses, regulator diaphragms, and in years gone by, stove windows and lamp chimneys. The value of sheet mica depends on the color, size, structure, and quality of the natural crystals. Quality of sheet mica varies widely within and between mica districts and even within a single deposit or mica-rich shoot.

A variety of synthetic materials—such as built-up mica, reconstituted and glass-bonded mica, organic polymers, and synthetic mica—and alternate materials—such as alumina ceramics, fused quartz, and talc—are replacing sheet mica in some uses. Technological developments, such as miniaturization of circuits and solid-state electronics, also reduce the need for sheet mica.

Muscovite in sheets as thin as paper is generally colorless, but thicker sheets may range from red or yellow brown to greenish brown or green. Reddish brown or ruby mica is generally thought to be of slightly better quality and brings a higher price than the other varieties of mica.

The best sheet mica is clear, flat, and free of mineral inclusions and structural defects. Mica that contains inclusions or impurities is called stained mica. Primary impurities are air bubbles, mottling, and mineral intergrowths; secondary impurities are air creep, clay, iron oxide and manganese oxide inclusions, and organic or vegetable stain.

Structural defects of the mica crystals are also of primary and secondary origins. The most common primary defects are reeves and wedge structure. Reeves are lines, striations, or shallow corrugations that lie in the plane of the cleavage. Where two sets of reeves intersect at an angle of nearly 60°, the resulting mica is said to have "A" structure. Wedge structure is caused by interlayering of sheets of unequal size. Some muscovite crystals, or books, have discontinuous sheets, partial intergrowth of sheets, or internal distortions and do not split freely. These books, termed "locky," or "tangled," are used only for scrap. Secondary structural defects include bending, cracking, twisting, and ruling, all caused by deformation of the mica after crystallization. Ruling is a secondary cleavage that cuts the basal cleavage at an angle of nearly 67°.

Crude books of mica must be at least 2 inches across to yield trimmed sheet mica. The average commercial book is about 5 inches across and about $\frac{1}{5}$ to $\frac{1}{2}$ as thick as it is wide. In some deposits books measuring 8 to 12 inches are common. Some larger books as much as several feet across and weighing 50–300 pounds have been found.

SCRAP MICA

Many pegmatite deposits contain only scrap-quality mica, and a large amount of scrap is produced during the mining, trimming, and fabricating of sheet mica. Such scrap is of high quality and is in great demand for making mica paper or reconstituted mica. Scrap mica obtained from clay or feldspar deposits or from mica schists is generally finely divided and is often called flake mica.

Scrap mica from sheet operations, from scrap mining, and from clay and feldspar mining may be blended before grinding to either dry-ground or wet-ground mica. Wet-ground mica is produced in chaser mills using wooden grinding surfaces. The finished product is usually white and has a greasy ungent feel and a pronounced sheen (Broadhurst and Hash, 1953, p. 9). Individual particles are highly polished and have smooth edges. Particle size generally ranges from 80 to 325 mesh. Wet-ground mica is used chiefly in the manufacture of wallpaper, rubber goods, and paint.

Dry-ground mica is produced in rod mills, hammer mills, cage disintegrators, and various types of attrition mills (Skow, 1962, p. 89). The product is a flat white powder having little luster; individual particles have rough edges and little polish. Particle size ranges from 20 to 250 mesh. Some special micronized mica has particle sizes of 1,000–3,000 mesh, or 5–20 microns. Dry-ground mica is used chiefly in the manufacture of rolled roofing or asphalt shingles, wallboard or joint cement, oil-well drilling mud, paint, rubber goods, plastic, and welding rods. The value of scrap mica depends on color and freedom from impurities. Various other mineral fillers can substitute for ground mica in most uses. Synthetic fluorophlogopite can substitute for scrap in reconstituted mica (Shell and Ivey, 1969, p. 214).

EXPLOITATION

Mica was mined in North Carolina, Virginia, and Alabama by the Indians more than a thousand years before the coming of the white man (Prufer, 1964,

p. 90), but modern mica-mining began in New Hampshire in 1803 and in North Carolina in 1867. The grinding of scrap mica began in a small way in North Carolina about 1870 (Broadhurst and Hash, 1953, p. 13) and grew rapidly after 1890.

In the United States, mica has been produced mostly in the Blue Ridge Mountains of North Carolina and in the Piedmont from Virginia to Alabama. Next in importance have been the New England States of New Hampshire, Maine, and Connecticut, and then the Black Hills of South Dakota. Smaller amounts have been produced in Colorado, Idaho, and New Mexico, and minor production is reported from Arizona, California, Montana, Nevada, and Wyoming. A few deposits are known in Maryland, Massachusetts, Minnesota, New Jersey, New York, Pennsylvania, Texas, Utah, Vermont, and Washington. North Carolina has been the principal producer of sheet mica and produces yearly 50–60 percent of the domestic scrap mica.

Because of the high cost of hand labor, the United States produces only a small amount of its domestic needs for sheet mica and relies on imports from India, Brazil, and Malagasy Republic for its principal requirements (fig. 50). In 1970, no production of sheet mica was reported in the United States for the first time in over 100 years, and it is unlikely that there will be much future production. U.S. imports of sheet mica have declined since 1950 because of the impact of improved technology and the availability of substitutes. In 1971, the Indian Government announced its decision to take over mica exports as of January 1972; the effects of this decision on the industry are not known.

The United States is the major producer (fig. 51) and consumer of scrap mica, including flake mica. Increased use of scrap probably depends on increased needs in housing for rolled roofing, joint cement, and paint.

North Carolina is the principal producer of scrap mica. Other States producing scrap in 1970 included Alabama, Arizona, Colorado, Connecticut, Georgia, New Hampshire, New Mexico, South Carolina, and South Dakota. Production for the rest of the world is mostly waste from the mining of sheet mica in India, Brazil, and Malagasy Republic.

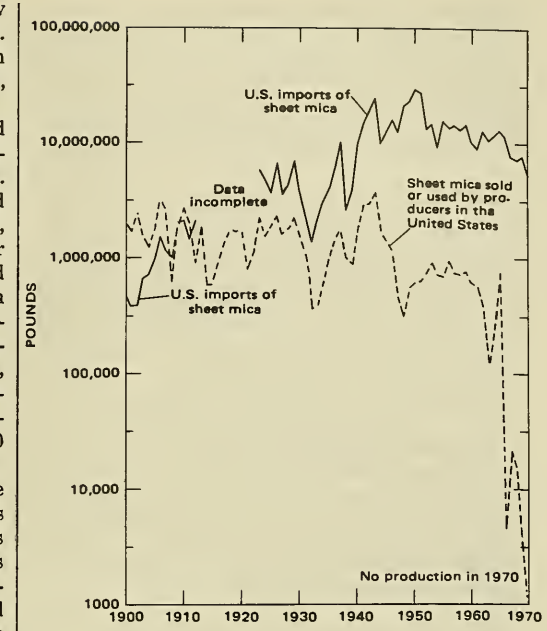

FIGURE 50.—Production of sheet mica in the United States compared with imports of sheet mica, 1900–70. Data from U.S. Geological Survey and U.S. Bureau of Mines, Mineral Resources of the United States and Minerals Yearbook, 1900–70.

MINING AND PREPARATION

Sheet-mica mining methods are simple and sometimes primitive. Most of the mines are small and shallow and require a minimum of equipment. Open-pit methods are used where possible, but most deposits are mined to some extent in underground workings that are generally irregular and follow the mica in rich shoots or from one rich pocket to another. Drilling and blasting must be done carefully to avoid damage to the mica. After a blast, crystals of mica are handpicked from broken rock. Large rocks are broken with sledges, and both waste and mica are usually hoisted to the surface. Because of the handwork involved, mining costs are high in relation to the average amount of sheet mica found in most deposits. Inefficiency and waste are common in mica mining. Handcobbed feldspar is sometimes recovered as a byproduct.

Processing of sheet mica requires extensive hand labor in cobbing or removing dirt or rock from the books, in rifting or splitting the books into thin sheets, and in trimming broken edges and imperfections from the sheets. Complete quantitative data are not available, but recovery of good trimmed mica from crude mica ranges from 2 to 8 percent for the average mine and is as much as 19 percent from good-quality crude mica in a few mines (Urban, 1932; Amos, 1959, table 1, p. 33).

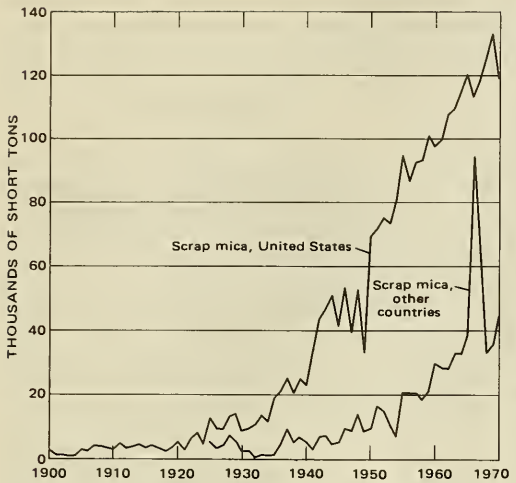

FIGURE 51.—Production of scrap mica in the United States, 1900–70, compared with that in the rest of the world, 1925–70. Data from U.S. Geological Survey and U.S. Bureau of Mines, Mineral Resources of the United States and Minerals Yearbook, 1900–70.

Details of the preparation and classification of mica and trade practices of the industry are too elaborate to discuss here, but they have been described well by Rajgarhia (1951), Skow (1962), Montague (1960), Jahns and Lancaster (1950), and Wierum and others (1938).

Most deposits of scrap mica must be deeply weathered so that they can be mined in bulk with power equipment and the ore can be washed and screened to recover the mica. The content of recoverable mica ranges from 3 to 20 percent. In simple washing plant operations, mica smaller than 8 mesh is not recovered readily; but through the use of spiral methods of concentration, better recovery is possible (Broadhurst and Hash, 1953, p. 6; Skow, 1962, p. 86).

PRICES

The selling price of mica ranges from only a few cents per pound for punch or scrap to many dollars a pound for large sheets of the best quality. In 1970, prices for sheet mica ranged from $0.85 a pound for sheets 1½ inches across to $8.00 a pound for sheets 8 inches or more across. Punch mica brought $0.07–$0.12 a pound. Scrap mica generally brought $30–$40 per short ton. Ground mica prices were $0.02–$0.04 a pound for dry-ground mica and $0.075–$0.095 a pound for wet-ground mica.

GEOLOGIC FEATURES OF MICA DEPOSITS

Sheet-muscovite deposits occur in coarse-grained igneous rocks called pegmatites; scrap-mica deposits are found in pegmatites, granite, and mica-rich metamorphic rocks. Phlogopite deposits are in pyroxenite layers in marble or gneiss.

PEGMATITES

Most pegmatites are light-colored coarsely crystalline igneous rocks, commonly found as dikes or sills in metamorphic rocks or in large granitic intrusions. Individual mineral grains and crystals range in length from less than 1 inch to many feet, and a large variation in grain size within a single pegmatite body is common.

Pegmatites range from small pods and thin seams to large masses hundreds of feet thick and thousands of feet long. In general, they are tabular or lenticular bodies. Some pinch and swell along strike or downdip, or both. Most lenticular bodies are discoidal, but some bodies are best described as tonguelike or pipelike. In some pegmatite districts, most of the deposits are concordant with the foliation of the enclosing country rock; in others, most are discordant bodies in joints or faults. Branching, folded, or irregular bodies may be present in areas of complex structure. Most elongate bodies and minor bulges or rolls in concordant pegmatites are generally parallel to the plunge of minor structural features in the country rock.

Pegmatites are composed mostly of feldspar, quartz, and mica but may contain accessory minerals such as garnet, tourmaline, apatite, and beryl and unusual or rare minerals of many types. The many and unusual minerals found in some pegmatites make pegmatites favorite collecting sites for mineralogists and rockhounds.

Plagioclase is generally the most common feldspar in muscovite-rich pegmatite. Perthite or perthitic microcline, an intergrowth of plagioclase and microcline feldspars, is generally present and may be abundant in some pegmatites. The feldspars are discussed in greater detail in a separate chapter.

Book mica in commercially mined pegmatite generally constitutes 2–6 percent of the rock. Local rich shoots or pockets might have as much as 40 percent muscovite, but large volumes of pegmatite have no more than 2 percent.

The minerals in many pegmatites are almost

evenly distributed throughout, but in other pegmatites the minerals are segregated into certain layers or parts of the body called zones. At places, these zones can be mined selectively to recover the desired minerals by hand sorting and are, therefore, important economically. In general, zones are successive shells, complete or incomplete, that commonly reflect the shape or structure of the whole pegmatite body. Where best developed, the zones are concentric about an innermost zone, or core, and according to accepted practice, the zones from the outermost one inward to the core are called border zone, wall zone, intermediate zones, and core.

Border zones are generally thin fine-grained selvages of quartz-mica-feldspar pegmatite; wall zones are of similar composition but are coarser grained. Intermediate zones may contain mixtures of several minerals or virtually all one mineral, usually feldspar. Most cores are a single mineral—commonly quartz or potash feldspar. The best quality and greatest concentration of sheet muscovite are commonly in the wall zone; less important concentrations are in intermediate zones and the core margin. In poorly zoned pegmatite, muscovite is scattered throughout the rock.

The principal mica pegmatite districts in the United States are in New England (Cameron and others, 1954), the Southeastern Piedmont from Virginia to Alabama (Jahns and others, 1952), the Blue Ridge Mountains in North Carolina (Lesure, 1968), the Black Hills of South Dakota (Page and others, 1953), and northern New Mexico (Jahns, 1946). Less important districts are in Idaho and Montana (Stoll, 1950), Colorado and Wyoming (Hanley and others, 1950), Nevada (Olson and Hinrichs, 1960), and California (Lesure, 1966). In India, the most important mica pegmatite districts are in Bihar, Madras, and Rajasthan (Skow, 1962; Rajgarhia, 1951). In Brazil, the important mica pegmatite districts are in Minas Gerais (Pecora and others, 1950). Important mica pegmatite districts are also known in Argentina, parts of Africa, the Soviet Union, and China (Skow, 1962).

The origin of pegmatites has been studied by hundreds of workers for more than 100 years. Jahns (1955) gives an extensive bibliography of these studies. Recent reports (Jahns and Tuttle, 1963; Jahns and Burnham, 1969) stress the origin of granitic pegmatite from crystallization of granitic magma in place in virtually a closed system with little or no wallrock alteration. In many districts, like the Black Hills of South Dakota, the spatial relationship between pegmatite and large masses of granite indicates the same or a similar source. In other areas, like parts of the Blue Ridge Mountains of North Carolina, no close relationship to granitic masses is evident, but the mica pegmatites are restricted to areas where regional metamorphism has reached at least kyanite or sillimanite grade.

PHLOGOPITE DEPOSITS

According to Hoadley (1960, p. 45), the occurrences and distribution of phlogopite deposits are everywhere similar. Known deposits are in areas of metamorphosed sedimentary rocks intruded by masses of pegmatite-rich granitic rocks. The phlogopite deposits commonly are in veins or irregular pockets in diopsidic pyroxenite interlayered with or cutting marble or gneiss. The pyroxenite may be normal intrusive mafic igneous rock or a contact metamorphic alteration of crystalline carbonate by solutions from granitic magma. The phlogopite deposits may also have formed by contact metamorphism at about the same time as the surrounding pyroxenite. The principal resources of phlogopite are in the Malagasy Republic (Murdock, 1963, p. 124–129); minor deposits are found in Canada (Hoadley, 1960), Mexico (Larrabee, 1946), Ceylon, and the Soviet Union (Skow, 1962). The United States has no commercial phlogopite deposits.

SCRAP- AND FLAKE-MICA DEPOSITS

The original source of scrap mica was the waste from sheet-mica mining and preparation, hence the name scrap. About 1910, however, demand for scrap had increased so much that mica deposits containing poor quality sheet or smaller sizes were being mined for just the scrap content. Today in Spruce Pine, N.C., which produces nearly half the scrap mica mined in the United States, deeply weathered alaskite bodies containing 10–20 percent muscovite are mined for fine-grained scrap mica or flake mica. In such deposits, depths to unweathered rock may be 50–100 feet for areas of several acres. Some deposits are mined for clay, and the mica is recovered as a byproduct; some are mined for mica, and the clay generally is lost in the washing process. Unweathered alaskite is mined for feldspar, and mica is recovered as a byproduct.

Flake mica can also be recovered from muscovite schist, a rock found in many metamorphic terranes. Such deposits may be a few tens or hundreds of feet thick and many miles long. Mica content can range from a few percent to at least 90 percent.

Many other minerals are commonly present, including quartz, feldspar, garnet, kyanite, and graphite. Most mica schist was originally fine-grained siltstone or shale, which was subjected to at least medium-grade regional metamorphism.

Where slightly weathered, mica schist can be easily mined. Recent work by the U.S. Bureau of Mines (Browning and Bennett, 1965; Adair and Browning, 1969) has developed methods of concentrating good-quality flake mica from mica schist. Preliminary studies in North Carolina indicate that the percentage of mica in schist ore is about four times as high as that of mica ores now being mined, and a flow sheet was developed that would make mica-schist products competitive in the present market (Lewis and others, 1971).

Another type of flake-mica deposit mined in Lancaster County, S.C., is very fine grained and claylike. The original rock, apparently a volcanic ash or tuff, has been altered to a mixture of sericite (fine-grained muscovite) and quartz. The rock is easily mined and requires minimum preparation for sale as a mineral filler.

Muscovite is one of the more stable rock-forming minerals and under ideal conditions will be concentrated in sediments. Such a deposit of detrital mica in Holocene sediments was mined in Davy Crockett Lake, Greene County, Tenn., from 1956 to 1960. The conditions of formation of this deposit are unusual; the lake is downstream from the washing and grinding plants of the Spruce Pine pegmatite district, and fine mica, which was lost in mining and processing of clay, feldspar, and scrap mica, collected in the headwaters of the lake. Similar deposits may occur elsewhere in the world where weathered metamorphic and igneous rocks are being eroded.

RESOURCES

IDENTIFIED AND HYPOTHETICAL RESOURCES

Few quantitative data are available to estimate reserves or resources of sheet mica. Most of the deposits mined to date were found by testing surface outcrops. Some mines have reached depths of 300–400 feet in the United States and as much as 800 feet in India. If the present surface is considered a random sample of what occurs at depth, then many pegmatites in the world do not crop out but are still within mining depth (less than 500 ft). On this basis, conditional and hypothetical resources of sheet mica in the United States probably are at least equal to the amount already mined—that is, about 75 million pounds of sheet mica in deposits similar to those mined but not exposed at the surface in the principal mica pegmatite districts mentioned previously. Unless the economics of sheet-mica mining change radically, little of this hypothetical mica will ever be looked for or mined. In case of a national emergency, initial demand for sheet mica will be filled by the Government stock piles (table 84).

TABLE 84.—*Sheet mica on hand in all U.S. Government inventories, as reported by General Services Administration, March 31, 1972*

[Classification: *block mica*, minimum thickness of 0.007 in. and minimum usable area of 1 sq in.; *film mica*, variable thicknesses ranging from 0.0012 to 0.004 in. and minimum usable area same as block mica; *splittings*, maximum thickness of 0.0012 in. and minimum usable area, for top qualities, of 0.075 sq in. (Skow, 1962, p. 4)]

Classification	*Weight (pounds)*
Muscovite block, stained and better	10,648,007
Muscovite block, nonstockpile grade	3,603,422
Muscovite film, 1st and 2d qualities	1,468,340
Muscovite film, nonstockpile grade	640
Muscovite splittings	37,630,606
Phlogopite block	16,721
Phlogopite block, nonstockpile grade	137,217
Phlogopite splittings	4,669,274

Resources of sheet mica also occur similarly in many countries throughout the world. Some of these are Canada, Guatemala, Argentina, Bolivia, Colombia, Austria, France, Norway, Rumania, the Soviet Union, Burma, China, Australia, and several small districts in Africa. The major resources of sheet muscovite, however, are in India and Brazil, and the major resources of phlogopite are in the Malagasy Republic. No quantitative data are available to estimate reserves or resources of sheet mica in these countries, but the resources in the Bihar and Madras areas of India are probably very large. Resources in Brazil, West Africa, Rajasthan area of India, and the Lake Baikal and Sayan Upland areas of the Soviet Union are large (Skow, 1962, p. 42). Resources in the other countries are small to moderate.

A few data are available to estimate resources of scrap mica. Although mica-rich zones in some pegmatite bodies may contain as much as 40 percent mica, the largest resources of scrap mica are in mica schists that may contain as much as 90 percent mica and in muscovite granites that contain 10–20 percent. Using a conservative figure of 40 percent mica, the average mica schist would contain 1,450 tons of mica per acre-foot of outcrop area. Mica schist formations are typically measured in tens or hundreds of feet in outcrop width and miles in outcrop length. Muscovite granites like the alaskite of Spruce Pine, N.C., or the granite of Stone Mountain, Ga., are principally a source of feldspar but contain 350–700 tons of byproduct or coproduct mica per acre-foot and have outcrops measured in many acres or square miles. Assuming a mining depth of 100 feet, the resources of scrap mica per

acre of schist would be 145,000 tons and of granite, 35,000 tons.

In areas where geologic and mining data are available, good estimates of resources can be made. Thus, reserves of primary scrap or flake mica in the Spruce Pine district have been estimated as 45–50 million tons in material similar to that currently being mined (Brobst, 1962, p. 15–16). Conditional and hypothetical resources of scrap mica in that district may be several times greater than reserves. Hypothetical resources of scrap mica in mica schist, weathered pegmatite, and granite in the rest of the Blue Ridge Mountains and Piedmont in the southeastern States must equal or be many times greater than the reserves in the Spruce Pine district.

Similarly immense hypothetical resources of scrap mica are present in pegmatites, granites, and mica schist in metamorphic and igneous terranes in New England; the Black Hills of South Dakota; the Llano area of Texas; the Rocky Mountains; isolated mountains in Arizona, Utah, and Nevada; parts of California; and other areas of the United States. However, projected annual demand in the United States for flake mica by the year 2000 ranges from 280,000 to 550,000 tons (Petkof, 1970, p. 1096); thus, the resources of just the Spruce Pine district seem adequate to meet the expected demand for years to come.

World resources of scrap mica in pegmatite, mica schist, and granite are probably at least of the same order of magnitude as the U.S. resources. Production of scrap mica outside the United States has come mostly from mine scrap, and deposits of flake mica are largely undeveloped. Scrap-mica reserves and resources in India must be very large; about 10 million tons of scrap were heaped near mines and factories in 1965 (W. R. Griffitts, written commun.). The other sheet-mica-producing countries must have similar supplies of scrap because world demand has generally been much less than United States demand.

SPECULATIVE RESOURCES

Even less can be said about speculative resources of sheet mica than about reserves and hypothetical resources. Commercial sheet muscovite is found only in pegmatite deposits, and most of the pegmatite districts in the world have probably been found. The chances of finding a large previously undiscovered district seem negligible because pegmatite minerals are coarse grained and so unusual that they are not easily ignored. The distribution of phlogopite deposits is probably less well known, but again, chances of finding a large undiscovered district seem poor. Speculative resources of sheet mica, therefore, are probably not large.

In contrast to speculative resources of sheet mica, those of flake mica are probably large. Large areas of metamorphic rock known to exist throughout the world have not been studied in enough detail to outline mica schist deposits that might be a source of flake mica. Deposits of hydrothermally altered rock containing fine-grained muscovite like that being mined in South Carolina may be widespread but have not been evaluated as a mica resource. Deposits of detrital mica similar to that mined in Davy Crockett Lake, Tenn., represent another type not exploited to any great extent. All such deposits may be very widespread and may represent large speculative resources of flake mica.

PROSPECTING TECHNIQUES

Most sheet-mica mines are in pegmatites that were found because they were exposed at the surface. Chips of coarse mica in the soil, exposures of massive quartz, or white clay weathered from a feldspar-rich zone are good signs of a potentially mica-bearing pegmatite. Prospecting consists of trenching, digging shallow pits, or sinking shafts or inclines in a pegmatite. The pegmatite is tested for mica concentrations along the contacts with wallrocks or in the different zones. In the past 20 years some drilling has been done, but generally, drilling only proves the presence or absence of pegmatite and reveals little about any mica that it may contain. Only by mining a large enough sample of mica-bearing pegmatite can the miner establish, from the size, quantity, and quality of the mica, feasibility of development of the pegmatite. Geologic mapping to determine structure and metamorphic grade of the country rock may help outline potential areas for prospecting. Most sheet-mica-bearing pegmatites not in granitic rocks are in metasedimentary rocks that are products of medium- to high-grade (kyanite- or sillimanite-grade) regional metamorphism. If there has been later deformation, the pegmatite may contain mica that is deformed and good only for scrap. Mapping and detailed study of pegmatites begun during World War II proved that reserves and resources can be calculated in zoned pegmatites if the geologic details are known (Cameron and others, 1949; Jahns, 1955; Norton and Page, 1956). Study of the use of geophysical or geochemical techniques in looking for concealed deposits should be made. Small positive geochemical anomalies of various trace elements have been found in gneiss and schist within

5–50 meters of pegmatite that is rich in potash feldspar and mica (Shmakin and others, 1971).

Most prospecting is still done by prospectors who have developed their own criteria for finding mica through years of experience. The success of the Indian mica industry is in part the result of low labor costs that have permitted intensive and continued prospecting for new deposits by individual prospectors. For every 100 pegmatites that the Indians find, however, only two or three prove rich enough to develop for commercial mining (Rajgarhia, 1951, p. 49). This ratio of productive to nonproductive pegmatites seems applicable to the world supplies.

PROBLEMS FOR RESEARCH

The principal problems of the mica industry are the high cost of hand labor needed for mining and processing of sheet mica and the increasing use of substitutes or decreasing need for sheet mica because of improved technology. The U.S. Bureau of Mines forecasts a drastic reduction in sheet mica needs by the year 2000 (Petkof, 1970, p. 1093), and there is little reason to believe that sheet-mica mining will ever again be important in the United States. With the decrease in mining and processing of sheet mica, the amount of high-quality scrap will also decrease. Increased use of synthetic mica as a substitute for coarser scrap in reconstituted mica can be expected. Large supplies of high-quality scrap probably will be available from India as long as the sheet-mica industry is active there. In the United States, a need for scrap- or flake-mica sources closer to the active industry could be met by continued evaluation of mica schist deposits that are outlined by regional geologic mapping.

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MOLYBDENUM

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ABSTRACT OF CONCLUSIONS

Molybdenum, a rare metal widely dispersed in the rocks of the earth's crust, occupies an essential place in today's highly sophisticated industries.

World production of molybdenum is about 200 million pounds per year, of which about 60 percent is produced in the United States. Identified resources amounting to about 17.5 million tons of molybdenum in the United States and about 32 million tons in the world and occurring both as the primary metal sulfide in large low-grade porphyry molybdenum deposits and as a subsidiary metal sulfide in large low-grade porphyry copper deposits, seem adequate to supply world needs for the forseeable future.

To assure economic availability of these resources and to discover additional resources that surely will be needed if world demand continues to escalate and if environmental problems should tend to restrict the commercial development of resources, employment of our most sophisticated exploration techniques will be essential. Successful prediction of the location of undiscovered molybdenum resources will depend upon an understanding of the genetic relationship of molybdenum to associated magmatic rocks, the environments in which these magmatic rocks were emplaced, and the role of plate tectonics in developing favorable environments and mechanisms for the generation and emplacement of molybdenum-carrying rocks.

INTRODUCTION

Molybdenum, discovered in the last 1770's, is a metal of fairly recent entry into the commercial market, having come into significant use during the 1920's as a result of extensive metallurgical research into its alloying properties and as a result of the establishment at Climax, Colo., of proved reserves sufficient to supply world demand for many years at a reasonable price. Its importance as an alloying metal is due chiefly to the increase in hardness, toughness, and resistance to corrosion and wear at elevated temperatures that it imparts to iron, steel, and stainless steel.

Molybdenum is a silvery-gray metal having a high specific gravity (10.2)—slightly higher than copper—and a melting point of 2,620°C—the fifth highest melting point of all metals. It is ductile and has a hardness of about 200 V.P.N. (Vickers Pyramid Number) and its coefficient of thermal expansion is among the lowest of metals. It is resistant

to acids and oxidation at ordinary temperatures. It has a high thermal conductivity and good electrical conductivity.

The principal uses of molybdenum are in the iron and steel industries with 70 percent of the apparent consumption going into high-speed, tool, stainless, and low-alloy construction steels and 20 percent going into special alloys and castings; the remaining 10 percent is used as molybdenum metal and in pigment, catalysts, agriculture, chemicals, and lubricants.

It must be evident from the above list of uses that molybdenum is an essential metal in a highly sophisticated industrialized nation such as the United States and that it is equally essential in other industrially developed countries. The extent to which our present living standards depend on the ready availability and constant supply of molybdenum may be illustrated by an example of molybdenum utilization in the automotive industry: 10 million units yearly production consumes more than 2 million pounds of molybdenum, a significant consumption despite the small weight of molybdenum used per unit.

Without molybdenum as an alloying metal, superstrength steel as used in heavy construction such as modern skyscrapers and bridges would be more costly, and in some instances the increased weight needed for equivalent strengths would render certain construction patterns unmanageable.

Molybdenum can substitute for tungsten, vanadium, chromium, columbium, tantalum, nickel, and boron. Each substitution is a matter of cost-availability to obtain certain desired qualities in the finished product.

Molybdenum is virtually the sole metal commodity of which the United States is a net exporter. Domestic production in 1970 was just over 110 million pounds of molybdenum, or two-thirds of the free world production. Domestic consumption, on the other hand, is about 50 million pounds; the United States annually exports about 55 million pounds of molybdenum in various forms such as molybdenite concentrates, molybdenum trioxide, and ferromolybdenum to more than 20 other nations.

EXPLOITATION

Recorded world production of molybdenum began just after 1900, when about 100 short tons of the metal was produced, approximately half of which came from Australia and Norway and half from the United States (Fischer and King, 1964). Through the years, molybdenum has been produced, at one time or another, in some 30 countries around the world. The major part, however, has come from nine countries: the United States, Chile, Canada, Japan, Korea, Norway, Mexico, the U.S.S.R., and China.

The United States currently supplies about 60 percent of the world's total molybdenum; Canada, about 15 percent; the U.S.S.R. and China, about 15 percent; and all other producing countries, 10 percent.

World production of molybdenum increased from about 300,000 pounds per year in 1906 to 3 million pounds per year in 1932, a tenfold increase during this 26-year period. The next tenfold increase occurred within a 5-year period in the 1930's, as a result of a major increase in United States production brought about chiefly by the initiation of large-scale mining by block caving of the Climax ore body in Colorado. Production increased sharply during World War II to a high point in 1943 of 70 million pounds of molybdenum and then decreased rapidly to about 24 million pounds in 1946, remaining at this level until 1949 owing to the low level of demand that followed the end of hostilities. Since 1949 a relatively uniform and consistent increase in the annual rate of production, interrupted only by recession in 1958 and work stoppages in 1962, has continued to the present, at which time about 200 million pounds of molybdenum is produced annually.

Until 1936, domestic production of molybdenum was as a main product of molybdenum ores. In 1936, at the Bingham, Utah, porphyry copper mine, recovery of molybdenum as a byproduct was begun; today about one-quarter of the United States production of molybdenum is obtained as a byproduct of copper mining, and at least half of the world production of molybdenum is obtained as a byproduct or coproduct of copper mining operations.

For many years the famous Climax molybdenite mine in Colorado was the only known porphyry molybdenum deposit in the world; but in 1957, the Questa molybdenite deposit in New Mexico was recognized to have many characteristics of a stockwork-type ore body, and intensive exploration confirmed the presence of a large tonnage of low-grade molybdenite ore. In 1966, open-pit mining of the disseminated ore body at Questa began, and by 1969, the annual production of molybdenum was more than 10 million pounds. In British Columbia, several porphyry molybdenum and copper-molybdenum deposits were developed, and in 1966, molybdenum output from British Columbia's mines amounted to 20 million pounds.

Early in the 1960's, intensive exploration was

undertaken at the Urad-Henderson porphyry molybdenite deposits in Colorado. Production at the Urad mine began in 1967 at an annual rate of about 3 million pounds of molybdenum. In 1966, American Metal Climax, Inc., announced reserves of more than 300 million tons of ore in its Henderson deposit, some 2,000 feet below the Urad ore body, at a grade of 0.49 percent molybdenite. The company expects to put this mine into production by the late 1970's

Only at Climax, Colo., has the recovery of associated minerals in a porphyry-type molybdenum deposit so far been successful; tungsten (huebnerite), pyrite, topaz, uranium (brannerite), monazite, tin (cassiterite), and molybdenum oxide have been recovered as byproducts.

GEOLOGIC ENVIRONMENT

GEOCHEMISTRY [1]

Molybdenum is a metallic element of Group VIb of the periodic table and has atomic number 42, atomic weight 95.94, and occurs as six isotopes. In nature it has valences of +4 and +6 in molyhydrates and possibly rarely has valences in the +3 and +5 states. Molybdenum is a rare element, its abundance in continental crustal rocks being generally given as 1 to 1.5 ppm. It is rather uniformly distributed among the igneous rocks but averages slightly higher in basaltic rocks than in granitic rocks.

Chemically, molybdenum can function both as a metal and as a nonmetal. In the geochemical cycle it becomes concentrated in shales, clays, and phosphorites; in these rocks, there is a positive correlation between the content of molybdenum and the content of organic carbon. Molybdenum is also concentrated in coal and petroleum. Of the molybdenum that is supplied to ocean waters, virtually all is precipitated either mainly with the clay minerals or partly in hydrous manganese oxides.

Man's activities contribute molybdenum to the environment in mining, in metallurgical processing, in the addition of phosphate fertilizers to the soil, and in the conversion of coal and oil to provide for his various energy needs.

MINERALOGY

Molybdenum does not occur in nature in its free or native state but is found only in combination with other elements, such as sulfur, oxygen, tungsten, lead, uranium, iron, magnesium, cobalt, vanadium, bismuth, and calcium. The most common molybdenum minerals are molybdenite (molybdenum disulfide, MoS_2), powellite (calcium molybdate, $CaMoO_4$), wulfenite (lead molybdate, $PbMoO_4$), ferrimolybdite ($FeMoO_3 \cdot H_2O$), ilsemannite (molybdenum oxysulfate), and jordisite (amorphous molybdenum disulfide). Of these, only molybdenite, ferrimolybdite, and jordisite are of current economic importance. Some molybdenum has been recovered in the past, however, from wulfenite- and powellite-bearing ores. As the demand for molybdenum continues to rise, powellite, ferrimolybdite, and jordisite may be looked upon as possible source materials.

TYPES OF DEPOSITS

Molybdenum deposits are of five genetic types: (1) porphyry or disseminated deposits including stockworks and breccia pipes in which metallic sulfides are dispersed through relatively large volumes of altered and fractured rock, (2) contact-metamorphic zones and tactite bodies of silicated limestone adjacent to intrusive granitic rocks, (3) quartz veins, (4) pegmatites and aplite dikes, and (5) bedded deposits in sedimentary rocks.

PORPHYRY DEPOSITS

Probably more than 95 percent of the world's supply of molybdenum has been obtained from porphyry molybdenum or porphyry copper-molybdenum deposits. In these deposits primary copper sulfides and (or) molybdenite occur as disseminated grains and in stockworks of quartz veins and veinlets in fractured or brecciated, hydrothermally altered granitic intrusive rocks and in the intruded igneous or sedimentary country rocks.

Favorable host intrusive rocks with which the ore minerals are generally assumed to be genetically related range from intermediate to acidic and include diorite, quartz monzonite, and granite, and their porphyritic equivalents. Metalization commonly took place both in the host intrusive and in the surrounding or overlying country rock.

In the porphyry molybdenum deposits, molybdenite is characteristically the sole ore mineral. Molybdenite commonly is accompanied by pyrite, fluorite, and small amounts of tungsten, tin, lead, and zinc minerals. In contrast, the porphyry-copper or copper-molybdenum deposits contain only small amounts of molybdenum, and in these, the molybdenum is of economic significance only because of the recoverable copper content. The primary copper mineral is chalcopyrite, which is intimately associated with pyrite.

The porphyry or disseminated deposits are commonly considered to be pipe-shaped bodies, circular

[1] From material provided by Michael Fleischer, written commun., 1972.

or oval in plan and with steeply dipping sides. In nature, however, the deposits are more likely to be in complex forms, such as domal, funnel-shaped, arcuate, and annular bodies (Brown, 1969; James, 1971).

Almost invariably one or more major faults pass through or close to the ore bodies. Evidence of both preore and postore movement is abundant in these faults, and localization of the ore bodies along major faults is an accepted hypothesis. Intensive, widespread and continued fracturing of host intrusives and of enclosing country rocks is characteristic.

The average mineral content of porphyry-type deposits ranges from 0.1 to 0.5 percent molybdenite in molybdenum porphyries, and from about 0.015 to 0.1 percent molybdenite in copper-molybdenum porphyries. Currently minable porphyry deposits range in size from a few hundred feet to several thousant feet in horizontal dimension and may extend to depths of several thousand feet. Fractures and hydrothermally altered rocks extend many hundreds of feet outward beyond the limits of minable ore, decreasing in intensity outward from the central zone.

Three-fourths of the world's reserves of molybdenum are in the Western Cordillera of North and South America, the mountainous region along the western part of these continents. These reserves consist of large low-grade disseminated deposits of hydrothermal origin that occur in clusters throughout the length of the Cordillera. They are typical porphyry deposits, genetically associated with intrusive rocks of acidic to intermediate composition in areas of intense volcanism and complex tectonic history. The period of ore deposition extended from Late Triassic to middle Tertiary.

The remaining one-fourth of the world's reserves of molybdenum are distributed among the U.S.S.R., parts of Europe, southwestern Asia, and southeastern Asia including China, the islands of the South Pacific, and Australia; the U.S.S.R. reserves account for at least half of this fraction.

Porphyry or stockwork deposits that yield molybdenum alone or as the chief metal are known to occur principally in Alaska, British Columbia, and in the Rocky Mountain region of the United States (Clark, 1970); porphyry copper-molybdenum deposits from which molybdenum is obtained as a byproduct occur over the entire length of the Western Cordillera from Alaska to Argentina, and in other parts of the world (Eimon, 1970).

The Climax and Urad-Henderson deposits in Colorado and the Questa deposit in New Mexico are described here as three examples that illustrate the typical porphyry molybdenum ore deposits, their geological relationships, and the resources connected with this type of deposit. Comprehensive descriptions of the porphyry copper-molybdenum deposits in southwestern North America are given by Titley and Hicks (1966), and of those in the Western Hemisphere by Ridge (1972).

CLIMAX, COLORADO

For many years (1930–55), the Climax molybdenum deposit at Fremont Pass, about 100 miles west of Denver, Colo., was unique in that it was the only known porphyry molybdenum deposit in the world. Large-scale bulk mining of the disseminated ore body began in the mid-1930's, about 20 years after its discovery and after the mining from near the top of the deposit of small tonnages of high-grade zones that contained from ¾ to 1 percent molybdenite (Butler and Vanderwilt, 1933). The Climax mine, operated by the Climax Molybdenum Co. division of American Metal Climax, Inc., exploits one of the three largest known molybdenum stockwork deposits in the United States if not in the world. The two other deposits of equivalent size and character are the Questa molybdenum deposit in northeastern New Mexico (Molybdenum Corp. of America), and the Urad-Henderson molybdenum deposit at Empire, Colo. (Climax Molybdenum Co.). The Climax deposit has, according to the company's annual report, reserves amounting to about 500 million tons of molybdenum ore which contain over 2 billion pounds of molybdenum, sufficient to sustain the present rate of production through the remainder of this century.

The deposit consists of a complex dome-shaped mass of fractured, silicified, and mineralized Precambrian granite, gneiss, and schist that generally overlies a composite porphyry stock of quartz monzonite to granite composition, middle Tertiary in age. Molybdenite associated with quartz, pyrite, fluorite, topaz and lesser amounts of tungsten, scandium, titanium, and tin minerals is dispersed in fracture fillings, in veinlets, and as minute flakes throughout the fractured host rocks forming a low-grade (0.05 to 0.5 percent Mo) ore body of several thousand feet in smallest dimension. Several commodities, such as tungsten, pyrite, and tin, are recovered as byproducts. Climax has become a leading United States producer of tungsten in recent years. A small tonnage of monazite has been recovered in the past, as has a small amount of topaz. According to company reports, more than 150 million tons of ore had been mined from the Climax deposit by 1972. The ore deposit has not yet been

delineated completely and the possibility therefore exists that additional reserves may be discovered that will at least in part replace reserves currently being mined. Detailed descriptions of the geology of the Climax area and of the deposit were given by Vanderwilt and King (1955) and Wallace, Baker, Johnson, and MacKenzie (1960).

URAD-HENDERSON, COLORADO

The Urad-Henderson porphyry molybdenum deposit near Empire, about 50 miles west of Denver, is a prime example of the discovery and development of a huge deposit as a result of careful and exhaustive geologic study and the use of modern exploration techniques. The Urad ore body, known for many years, was first developed on high-grade quartz-pyrite-molybdenite fissures and fracture zones, from which about half a million pounds of molybdenum was produced during the early part of the century and in the 1940's. The Urad molybdenite ore body is localized in a zone of fractured and altered granite around the southern margin of a composite granite porphyry stock (Carpenter, 1960, p. 321) of middle Tertiary age. Molybdenite also occurs in veinlets and as disseminations in the altered and fractured granite between the fracture zones and fissures, forming a massive porphyry type body of many millions of tons of molybdenite ore containing from 0.3 to 0.5 percent molybdenite.

About 2,000 feet below the Urad ore body, and separated from it by altered rocks that contain only traces of molybdenite, is the Henderson molybdenite ore body. According to the Climax Molybdenum Co., reserves in the Henderson ore body amount to over 300 million tons at a grade of 0.49 percent molybdenite. Very few geological data have been published on the Henderson deposit, but it is a typical porphyry or stockwork deposit. The mine is expected to be brought into production late in the 1970's, with a planned milling capacity of 50,000 tons per day.

QUESTA, NEW MEXICO

Molybdenite at Questa occurs in massive quartz veins, in a stockwork of discontinuous veinlets, and as fine disseminated flakes in a hydrothermally altered and fractured zone several thousand feet wide. The quartz-molybdenite veins exploited during the earlier development period, as well as the stockwork molybdenite, lie along the contact of a composite intrusive body of granite and the overlying andesitic volcanic rocks. Molybdenite is the only mineral of economic importance in the deposit although rhodochrosite, fluorite, and a little chalcopyrite are present. The grade of the ore body is low, averaging only about 0.1 percent molybdenum. According to company reports, more than a quarter of a billion tons of ore has been developed at the property. Despite its low grade, the Questa deposit promises to be one of the major domestic sources of molybdenum for many years.

CONTACT-METAMORPHIC DEPOSITS

In the molybdenum-bearing contact-metamorphic deposits (tactites and skarns), molybdenite is commonly associated with scheelite, bismuthinite, or copper sulfides in zones of silicated limestone near granitic intrusive rocks. Molybdenite also occurs alone in contact-metamorphic deposits. The Pine Creek mine in California is an example of the contact type of deposit from which molybdenum and tungsten have been recovered as coproducts since 1939 (Bateman, 1956).

Significant amounts of molybdenum also occur in contact-metamorphic deposits in the northeastern Caucasus of the U.S.S.R., in China, and in Morocco (Kruschov, 1959). The molybdenite deposits of the Knaben mine in Norway are in quartz-rich amphibolitic gneisses of probable sedimentary origin and may be included in this category. The ore ranges from 0.1 to 0.2 percent molybdenite, and although production from the deposit has been persistent for many years, it has been relatively small.

QUARTZ VEINS

Quartz veins containing molybdenite are widely distributed throughout the world. Early production about 1900 was made from the relatively high grade deposits of this type. A prime example of vein type bodies is found at the Questa molybdenite deposit at Red River, N. Mex., where small tonnages of molybdenite were produced between the 1920's and the mid-1950's from high-grade quartz-pyrite molybdenite gash veins along the contact between a sodic granite and overlying andesitic volcanic rocks. The molybdenite content of the veins ranged from 1 to 30 percent molybdenite. Not until the late 1950's was it discovered that the veins were associated with mineralized rocks having the characteristics and potential for a large low-grade porphyry-type molybdenite ore body associated with a composite granite stock.

PEGMATITES

Commonly, pegmatite bodies and aplite dikes contain molybdenite among many other metallic and

nonmetallic constituents. The molybdenite is generally coarsely crystalline, occurring as rosettes or thick books and aggregates of flakes, which are erratically distributed in the host rocks. Although much specimen material of excellent quality can be obtained from this type of deposit, few deposits have been of economic interest owing to the characteristically small tonnage available and the erratic distribution of molybdenite. Notable among the pegmatite-type deposits that have yielded significant quantities of erratically disseminated molybdenum are those at Val d'Or and Preissac, in eastern Quebec, where molybdenite is associated with bismuth in pegmatite bodies and greisen zones (Vokes, 1963).

BEDDED DEPOSITS IN SEDIMENTARY ROCKS

Although molybdenum is concentrated in coals, shales, and phosphorites, no molybdenum of economic grade has been found in these rocks. Only in certain lignitic sandstone beds of southwestern North Dakota, northwestern South Dakota, and eastern Montana, and in some arkosic sandstone beds in the badlands of southwestern South Dakota and northeastern Utah, has the molybdenum content approached ore grade (0.1 to 0.2 percent Mo) in deposits thick enough to be minable.

In the United States, molybdenum is associated in significant amounts with some of the bedded sandstone uranium deposits in Arizona, Wyoming, South Dakota, New Mexico, and Utah, and in the Gulf Coast region of Texas. Similar occurrences undoubtedly exist in other parts of the world, but published data are not readily available on these deposits. The molybdenum is in the minerals jordisite and ilsemannite and is present in amounts ranging from a few parts per million to more than 0.5 percent. It is irregularly distributed with respect to the uranium ore bodies, commonly occurring along or some distance from the outer margins of the ore bodies rather than within them. Ordinarily the small amount of molybdenum present in this type of ore deposit is detrimental because the molybdenum interferes with the recovery of uranium and must be segregated out of the circuits during milling processes. However, where the uranium deposits are of sufficient size and the molybdenum content is significant, a valuable byproduct may exist. According to the U.S. Bureau of Mines, molybdenum has been recovered from composites of uranium ores and ash residues of some uranium-bearing lignites from South Dakota and New Mexico.

RESOURCES

IDENTIFIED AND HYPOTHETICAL RESOURCES

About half the world's identified resources of molybdenum are in the United States, and of these resources, about 75 percent occur in deposits where molybdenum is the principal metal sought. The other half of the world's identified resources are distributed among more than 30 countries around the world. These resources occur as large bodies of fairly uniformly mineralized rock containing more than 500 ppm (parts per million) (0.05 percent) of molybdenum if no other valuable metal is present in significant amounts, or more than 50 ppm (0.005 percent) of molybdenum if molybdenum is not the primary metal sought.

Most of the identified resources of molybdenum are in the disseminated or porphyry-type deposits of the Colorado Mineral Belt, the Sangre de Cristo Range in New Mexico, and the Basin and Range province of the southwestern United States; the Interior Belt of British Columbia, Canada; the Andean Cordillera of Peru and Chile; and the Ural and Altai Mountains of the U.S.S.R. (table 85). Many of these deposits have been explored only to a minimal extent, and the metal contents appear to be lower than current ore grades—molybdenum in porphyry molybdenum deposits in the order of 0.01 to 0.1 percent and copper in porphyry copper-molybdenum deposits in the order of 0.1 to 0.2 percent—too low to be profitably mined under present conditions.

The magnitude of the identified resources of molybdenum can only be partly estimated directly from published data and statistics, because of the large fraction that is associated with copper resources. Clearly a sizable part of the discussion of the resources of molybdenum must therefore be based on geologic and geochemical information.

Large quantities of molybdenum probably are still hidden in areas of known deposits, as extensions of mining districts or mineral belts, and occur in deposits similar in geologic character and grade to those already known. Such hypothetical resources are predicted on the basis of known distributions of geologic environments favorable for molybdenum deposits and on the basis of our current understanding of the processes of deposition of molybdenum deposits. The bulk of hypothetical resources thus estimated amounts to about 1 billion tons of molybdenum, a large part of which appears to be equally divided between the United States and the U.S.S.R.

Table 85 is a summary of the estimated world resources of molybdenum.

TABLE 85.—*Estimated magnitude, in millions of pounds, of world resources of molybdenum*

Area	Identified resources [1]	Hypothetical resources [2]
North America:		
Canada:		
British Columbia	8,000	
Quebec	2,000	
Subtotal	10,000	10^5
Greenland	200	
United States:		
Alaska	1,000	
Arizona	2,000	
Colorado	20,000	
Idaho	1,000	
Maine	100	
Montana	1,000	
Nevada	500	
New Mexico	8,000	
North Carolina	100	
Texas	100	
Utah	1,000	
Washington	200	
Wyoming	100	
Subtotal	35,100	10^6
Puerto Rico	500	
Mexico	1,000	
Central America	1,000	
Total	47,800	10^4
South America:		
Argentina	100	
Columbia	100	
Ecuador	100	
Chile	5,500	
Peru	1,300	
Total	7,100	10^5
Europe:		
Bulgaria	100	
Rumania	100	
Spain	100	
Yugoslavia	1,000	
Total	1,300	10^4
Africa:		
Morocco	50	
Sierra Leone	50	
Total	100	10^3
Asia:		
Burma	100	
China	1,000	
India	50	
Iran	100	
Japan	100	
U.S.S.R.	5,000	
Thailand	50	
Vietnam	50	
Total	6,450	10^6
Antarctica	50	10^2
Australia	100	10^3
Oceania:		
Borneo	30	
Bougainville	40	
New Guinea	30	
Philippines	100	
Total	200	10^4
World total	[3] 63,100	[4] 2.2×10^6

[1] Identified resources are specific, identified mineral deposits that may or may not be evaluated as to extent and grade, and whose contained minerals may or may not be profitably recoverable with existing technology and economic conditions.
[2] Hypothetical resources are undiscovered mineral deposits, whether of recoverable or subeconomic grade, that are geologically predictable as existing in known districts.
[3] Equal to 31,550,000 tons.
[4] Equal to 1.1 billion tons.

SPECULATIVE RESOURCES

Speculation as to worldwide distribution and magnitude of molybdenum resources necessarily must be based on geologic relationships of the deposits that are best documented and most clearly understood. Domestic deposits offer the best information in this regard; consequently models based largely on occurrences in the United States and the Western Hemisphere as described under "Porphyry Deposits" are used to infer speculative resources.

World molybdenum resources are likely to be divided somewhat equally between deposits that contain molybdenum as the primary metal and those in which molybdenum is expected to be a byproduct or coproduct. Porphyry-molybdenum and porphyry-copper deposits are expected to contain by far the bulk of molybdenum resources.

Porphyry-molybdenum or porphyry-copper deposits are individual mineral deposits associated with stocklike intrusives, breccia structures, and faults. Distribution of this type of deposit worldwide, therefore, should be related to the distribution of certain major geologic features:

1. The deposits are found in belts of Cretaceous-Tertiary tectonic activity that were disturbed by subsequent igneous activity (Eimon, 1970). They occur along the cordillera of North and South America, the Alpide belt (Sillitoe, 1972), the Iranian orogenic belt, the south Pacific Arc, and in the Ural and Altai Mountains of the U.S.S.R.
2. They are associated mostly with intrusive activity that ranges in age from Triassic to mid-Tertiary (Sillitoe, 1972).
3. They occur in intrusive rocks of intermediate to acid composition; porphyry molybdenum deposits tend to be associated with granitic intrusives and porphyry copper-molybdenum deposits with instrusives of intermediate composition.
4. The molybdenum deposits commonly occur in clusters or groups of 5 to 20 miles in radius (King, 1970).
5. Porphyry deposits are commonly found in areas of gravity and magnetic lows; porphyry molybdenum deposits related to Tertiary silicic intrusives tend to occur in regional gravity lows.
6. Molybdenum deposits are commonly alined in major structural belts and at intersections of structural belts (Noble, 1970).
7. The intrusive rocks and commonly the intruded rocks show evidence of local and regional frac-

turing of an intense nature and of long duration (Rehrig and Heidrick, 1972).

8. The deposits are associated with intrusives of a complex nature showing evidence of multiple intrusion events (Wallace and others, 1968).
9. Intense hydrothermal alteration of host intrusive as well as of country rocks with an accompanying variety of accessory minerals is a trademark of porphyry deposits (Vanderwilt and King, 1955).

Using a combination of some of the geologic features just described, we have estimated speculative resources of molybdenum in and near the State of Colorado as an example.

The known molybdenum occurrences in and near Colorado occur in clusters that are shown in figure 52. These clusters of molybdenum deposits are closely associated with areas of principal middle Tertiary silicic intrusive activity. The molybdenum occurrences and associated intrusives are spatially related to major gravity lows, also shown in figure 52.

Three of the clusters of molybdenum occurrences contain the major porphyry molybdenum deposits at Henderson, at Climax, and at Questa. Some evidence suggests that the other clusters shown may

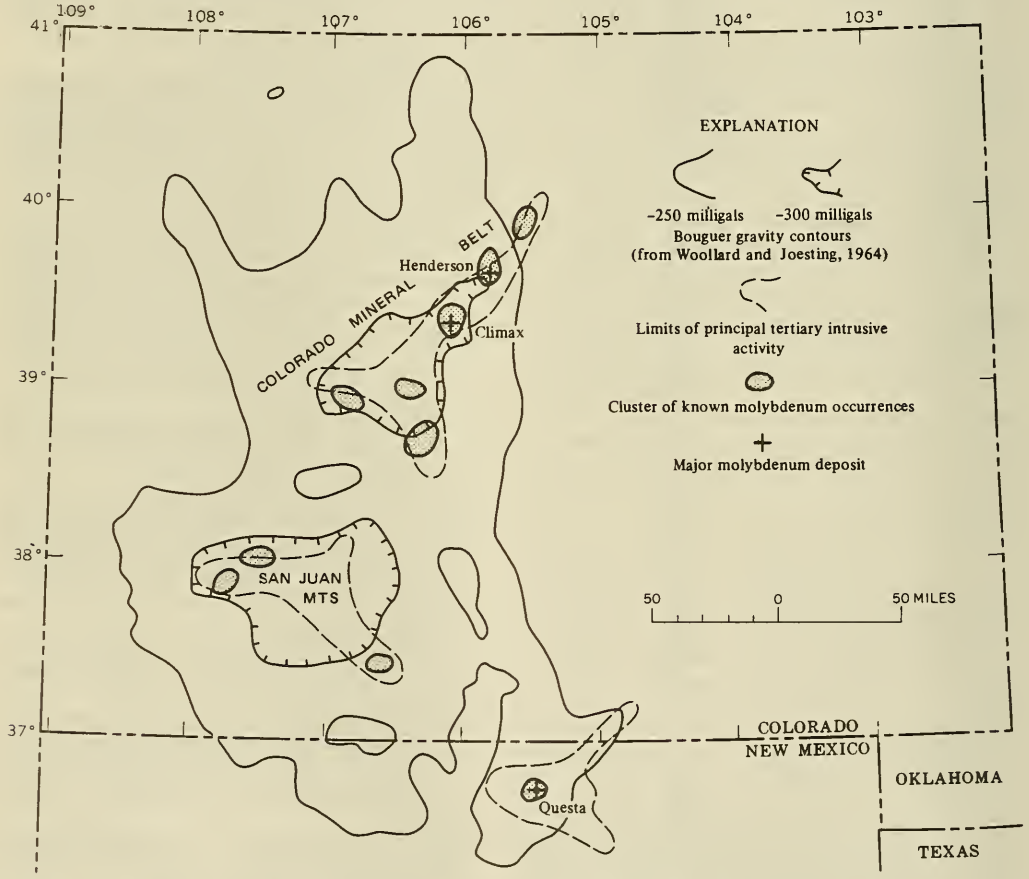

FIGURE 52.—Map showing location of molybdenum resources in Colorado and northern New Mexico in relation to various geologic parameters.

also contain major molybdenum deposits, though perhaps not all of minable grade. For example, the cluster of occurrences next southwest of the Climax cluster has been drilled by exploration companies for many years, and although no minable deposit has been discovered, a phenomenal amount of widely dispersed molybdenum has been revealed, probably greater in amount than is contained in the Climax deposit itself (Ogden Tweto, oral commun., 1972). From a geological standpoint, but not an economic standpoint at this time, this cluster contains a major molybdenum deposit.

Molybdenum deposits known in the San Juan Mountains in southwestern Colorado occur largely in the volcanic pile overlying the intrusive bodies that form the roots of the present San Juan volcanic field. Deposits in central Colorado in the main segment of the Colorado Mineral Belt are associated with intrusive bodies that represent the root-zone of a volcanic field now largely stripped away by erosion. If major molybdenum deposits occur in the San Juan field, presumably they lie at depth in the root-zone of the present volcanic pile, analogous to the central Colorado deposits. Occurrences known at the surface in the San Juan field are likely "leakages" from deeper seated deposits. The geological probability of major molybdenum deposits at depth in the San Juan Mountains seems good, although the economics of mining them, even if they could be found now, are at present unfavorable.

The three known major molybdenum deposits in and near Colorado have produced or contain unmined resources estimated at 5×10^9 lbs molybdenum each. Returning to the earlier conclusion that each of the 10 clusters of molybdenum occurrences shown on the map likely contains a major molybdenum deposit, we can estimate a total resource for the map area of roughly 5×10^{10} lb molybdenum, occurring in the vicinity of surface occurrences of molybdenum.

By making further assumptions that volcanic and other young rocks in the San Juan Mountains and in the vicinity of Questa may cover unknown clusters of molybdenum occurrences and that the spacing of clusters of molybdenum occurrences in the root-zone of a middle Tertiary igneous province is similar to that shown in the central Colorado part of the Colorado Mineral Belt where a root-zone is exposed, it is logical to infer the presence of additional unknown clusters in the San Juan Mountains and in the vicinity of Questa. Such unknown clusters may nearly equal in number those already known at the surface, judged from the areas of possible molybdenum occurrence implied by the outlines of gravity lows and of middle Tertiary intrusive activity shown on the map. If this assumption is correct, perhaps about 20 major molybdenum deposits exist in and near Colorado, representing a total resource of roughly 10^{11} lb molybdenum.

PROSPECTING

The search for molybdenum is facilitated by the physical properties of molybdenite as well as by the geochemical characteristics of the element. Molybdenite does not oxidize readily, and because of its bright silvery gray color and a strong platy crystal habit, it can be seen by eye in concentrations amounting to less than 100 ppm in light-colored rocks. Molybdenum is a mobile element and is both sulfophile and oxyphile. These characteristics work both for and against the prospector. In chemically acid environments, as in the presence of pyrite, molybdenite commonly is fixed in place, chiefly as ferrimolybdite, a recognizable molybdenum mineral, but also very commonly is attached to iron-bearing clay minerals, and to goethite and other limonitic minerals, in which forms it is not ordinarily recognizable. Fortunately, molybdenum in its six-valence oxidation state is amenable to inexpensive and rapid detection by qualitative and semiquantitative chemical and spectroscopic methods that have threshold sensitivities in the parts per million range, approaching and even reaching crustal-abundance values of molybdenum. In chemically less acid environments or in alkaline environments, molybdenite may convert to ilsemannite, a water-soluble blue efflorescence.

Because the economically significant molybdenum deposits of today, and probably of the foreseeable future, are the large volume stockworks and porphyry-type deposits related to fractured and hydrothermally altered granitic intrusive rocks, various geophysical techniques are useful prospecting methods (Sumner, 1969). Anomalously low magnetism may be detected as a result of the removal of magnetite during hydrothermal alteration of host intrusives, and low gravitational anomalies due to large intrusive stocks of granitic rocks may be measurable.

In terranes that are characterized by large volumes of silicic intrusive rocks as young as Tertiary in age, such as the Western Cordillera of the United States, low regional gravity values are closely correlated with distribution of the young silicic rocks; because molybdenum seems to be preferentially concentrated around silicic intrusives of Tertiary age in this region, major regional gravity lows reflect regions favorable for molybdenum deposits. In

terranes characterized by large volumes of silicic rocks older than Tertiary, such as British Columbia, low regional gravity values are not correlated closely with the distribution of the silicic rocks; inansmuch as molybdenum is associated principally with Mesozoic intrusives in British Columbia, major regional gravity lows do not correlate closely with regions of known molybdenum deposits.

Residual heat in intrusive rocks, heat from exothermal weathering of sulfides, and differences in vegetative cover due to metal concentration and alteration may be detected by airborne infrared imagery techniques, but these methods are not adequately developed to date to be highly useful in exploration. Geochemical and biochemical sampling of vegetative cover, soils, rocks, and water have been used to delineate general target areas of molybdenum concentration at and near ground surface.

PROBLEMS FOR RESEARCH

Because economic exploitation of molybdenum today requires that large tonnages of ore be mined and processed, large surface areas will be disturbed whether mining be done by underground methods or by open-pit methods; and because of the low mineral content of the ores, large surface areas will be needed for disposal of the residual waste materials. Molybdenum exploitation therefore is subject to the same or similar environmental problems as any large-scale operations, whether it be strip mining of coal, stone quarrying, mining of beach-sand deposits, or opencut mining of iron, aluminum, and copper.

Successful prediction of the location of presently unknown molybdenum deposits will come mostly from improved understanding of (1) the genetic connection between molybdenum (as well as associated elements) and the magmatic rocks around which molybdenum deposits formed, (2) the environments in which the magmatic rocks were generated and emplaced, and (3) the role of plate tectonics in developing favorable environments for generation and emplacement of molybdenum-carrying magmatic rocks.

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NICKEL

By Henry R. Cornwall

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ABSTRACT OF CONCLUSIONS

At the present time the free world requirement of nearly 1 billion pounds of nickel per year is supplied from deposits of nickel sulfides, mostly in Canada, and of nickel laterites, mainly in New Caledonia. World resources from these types of deposits are estimated to total 70 million tons (140 billion pounds) of nickel in 7 billion tons of material averaging about 1 percent nickel. An additional 7 billion tons averaging 0.2 percent nickel, or 14 million tons of nickel, is estimated for sulfide deposits in the United States. The 0.2–0.4 percent of nickel universally disseminated in peridotites and serpentinites throughout the world amounts to a figure several orders of magnitude greater than 70 million tons, as does the quantity of nickel contained in deep-sea mangenese nodules; but new technological developments will be required to recover nickel successfully from these two types of occurrence. The discovery in 1949 at Thompson, Manitoba, of a major new type of nickel sulfide deposit suggests the possibility that similar deposits may exist elsewhere in the world.

INTRODUCTION

Nickel is vital to the economic welfare and security of the United States, as it is also to the other industrial nations of the world. This is illustrated by examining the uses of nickel. In 1970 (U.S. Bureau of Mines, 1970, Minerals Yearbook) the United States consumption was:

Use	*Consumption (million pounds)*
Steel	124
Super alloys	23
Nickel-copper alloys	13
Permanent magnet alloys	5
Other nickel alloys	71
Cast irons	10
Electroplating	50
Chemicals	2
Other	14
Total	312

Free world consumption (Metals Week, Jan. 3, 1972) in 1970 and 1971, by area, was as follows:

	Consumption (million pounds)	
Area	*1970*	*1971*
Western Europe and United Kingdom	376	327
United States	330	273
Japan	202	172
Canada	33	24
Australia	9	9
Other	25	20
Total	975	825

The United States obtains most of its nickel from foreign sources—mainly Canada. Since 1966 the primary production of nickel in the United States has averaged 26 million pounds per year. The remainder of the nickel consumed has come almost entirely from Canada. The United States is thus almost completely dependent on foreign sources of nickel under present economic conditions.

EXPLOITATION PROBLEMS

Exploitation problems in nickel mining and processing are in part the same as or similar to those for copper. Air pollution is a major problem around the smelters, and it is likely that strict controls on smoke exhalations will soon be enforced throughout the United States. Most other countries are less concerned with air pollution at the present time, but demands for stricter control are also increasing in those countries.

Another major consideration, particularly applicable to some areas of large potential laterite development, is that the political climate of some countries is not conducive to huge long-term investment (hundreds of millions of dollars) and a long development period (5 years or more for a large operation).

The cost and difficulty of recovering nickel-bearing nodules from mid-ocean depths of 3,500–4,500 meters are major problems. Furthermore, suitable refining methods have yet to be demonstrated. The availability of large and relatively low-cost sources of the component metals on land also reduces incentive to their development.

GEOLOGIC ENVIRONMENT

GEOCHEMISTRY

Nickel is widespread in nature and is estimated to be the fifth most abundant element of the earth. Estimates of the nickel content of the earth's crust range from 0.008 to 0.02 weight percent (Fleischer, 1953). Ultramafic igneous rocks—dunite, peridotite, and pyroxenite—contain the most nickel, 0.1–0.3 percent; Vinogradov (1956) estimated the average nickel content of these rocks to be 0.12 percent. His estimates for other rock types are: mafic igneous rocks (basalt, gabbro, norite, and related rocks), 0.016 percent; neutral igneous rocks (diorite and andesite), 0.0055 percent; silicic igneous rocks (granite, rhyolite, and related rocks), 0.0008 percent; and sedimentary rocks (clay and shale), 0.0095 percent.

A generally accepted theory is that the core of the earth, 4,300 miles in diameter, has a composition similar to that of iron meteorites, most of which are kamacite—native iron with a nickel content of almost 7 percent. Inasmuch as the margin of the core is 1,800 miles below the earth's surface, this vast amount of nickel will probably never become available to man. The crust of the earth (about 10 miles thick), from which man must obtain the nickel he needs, contains only 0.003 percent of the total nickel in the earth, as computed from data given by Mason (1958, p. 44, 50).

The mantle, lying between the crust and the core of the earth, is nearly 1,800 miles thick and is believed to be peridotitic. Rocks of this ultramafic zone, like similar rocks exposed at the surface, may contain 0.1–0.3 percent nickel. Because the mantle makes up more than two-thirds of the total mass of the earth, it probably contains a large quantity of nickel.

The peridotite and related mafic rocks that have intruded the crust of the earth, and are in part exposed at the surface, probably have been derived largely from the mantle. Furthermore, most of the known nickel ore deposits are closely associated with mafic and ultramafic intrusive rocks, and the nickel in the ore bodies was probably derived either from the intrusives themselves or from similar rocks at depth. Thus the original source of most of the nickel ore bodies found in North America and elsewhere in the world was probably the mantle.

NICKEL MINERALS

The nickel minerals are given in table 86. The nickel-iron sulfide pentlandite [$(Fe,Ni)_9S_8$] is the principal present economic source of nickel, and garnierite (nickel-magnesium hydrosilicate) is next in economic importance. Garnierite—also called nickel gymnite, genthite, noumeite, and nepouite—

TABLE 86.—*Nickel minerals*

Mineral	Formula	Occurrence
Native nickel-iron	Ni_3Fe	Rare.
Pentlandite	$(Fe,Ni)_9S_8$	Common.
Bravoite	$(Fe,Ni)S_2$	Minor; secondary.
Violarite	Ni_2FeS_4	Do.
Vaesite	NiS_2	Rare.
Polydymite	Ni_3S_4	Do.
Millerite	NiS	Minor; secondary.
Heazlewoodite	Ni_3S_2	Rare.
Siegenite	$(Ni,Co)_3S_4$	Minor.
Linnaeite	$(Co,Fe,Ni)_3S_4$	Do.
Gersdorffite	NiAsS	Do.
Niccolite	NiAs	Do.
Rammelsbergite	$NiAs_2$	Rare.
Chloanthite	$(Ni,Co)As_{3-x}$	Do.
Smaltite	$(Co,Ni)As_{3-x}$	Do.
Skutterudite	$(Co,Ni)As_3$	Do.
Maucherite	$Ni_{11}As_8$	Do.
Breithauptite	NiSb	Do.
Ullmannite	NiSbS	Do.
Parkerite	$Ni_3Bi_2S_2$	Do.
Annabergite	$Ni_3(AsO_4)_2 \cdot 8H_2O$	Rare; secondary.
Morenosite	$NiSO_4 \cdot 7H_2O$	Do.
Zaratite	$NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$	Do.
Garnierite	Nickel-magnesium hydrosilicate	Common; secondary.

is not a true mineral but rather a mixture of nickel serpentine, nickel talc, and possibly other silicates.

Besides the nickel mnierals given in table 86, nickel occurs in minor amounts in pyrrhotite ($Fe_{1-x}S$) and pyrite (FeS_2), particularly where these sulfides are associated with mafic or ultramafic rocks. In most of these occurrences the total amount of included nickel is less than 1 percent. Nickel may replace iron to a considerable extent in these minerals, but substantial amounts may also be present as intergrowths of pentlandite or other nickel sulfides. Native terrestrial iron also contains nickel, ranging in amounts from 2 to 75 percent, but such native nickel-iron is rare; it occurs in basalts and carbonaceous sediments and with limonite and organic matter in petrified wood. The most important occurrence of native terrestrial iron is on Disko Island, Greenland, where it occurs in basalt as particles and, in places, as masses as large as 20 tons.

TYPES OF DEPOSITS

Sulfide deposits are by far the most important present source of nickel, in regard to both quantity of nickel and number of deposits. In 1964 two sulfide districts in Canada were producing about 80 percent of the free world total; one of these, the Sudbury district, has produced more than half the total world supply since about 1905. In recent years, however, major deposits have been discovered in other parts of the world, particularly in Australia and South Africa, as well as two large but very low grade deposits in the United States.

Another type of deposit, in which sulfides (together with arsenides of nickel, cobalt, and copper) occur in hydrothermal veins, has been found in both Canada and the United States, but these deposits are small and unimportant as sources of nickel.

Important nickel deposits are found in the lateritic mantles formed by the weathering of peridotite, include dunite, pyroxenite, and serpentinite, mostly in tropical and subtropical climates. The weathering of fresh peridotite has yielded nickel-silicate laterites in which the hydrosilicate garnierite is the principal nickel mineral. These deposits contain more than 1.5 percent nickel. Large deposits of this type occur in New Caledonia, and medium to large deposits occur in Indonesia, Venezuela, Brazil, United States (Oregon), and elsewhere. The weathering of serpentinite (serpentinized peridotite) has also formed nickeliferous iron laterite that averages 0.9–1.4 percent nickel. Large deposits of this type occur in Cuba and the Philippines, and medium to large deposits occur in Indonesia, the U.S.S.R., the Western United States, Guatemala, and other localities.

Recent oceanographic research has revealed the presence of vast deposits of nickel-bearing manganese-oxide nodules on deep ocean floors, particularly in the Pacific Ocean. The nodules contain 0.1–1.1 percent nickel as well as somewhat lesser amounts of copper and cobalt.

Most of the nickel deposits of the world that were known as of 1950 were shown by the U.S. Bureau of Mines (1952, fig. V–1), but since then, major deposits have been discovered in the United States, Canada, Australia, Guatemala, Colombia, and South Africa.

SULFIDE DEPOSITS

The nickel-bearing sulfide deposits typically consist predominantly of pyrrhotite ($Fe_{1-x}S$) and associated pentlandite [$(Fe,Ni)_9S_8$] and chalcopyrite ($CuFeS_2$). Many of the deposits contain minor but recoverable amounts of platinum metals, cobalt, and selenium. These deposits occur in or near peridotite or norite intrusions and are generally considered to be genetically related to them. The sulfides occur as disseminations, massive bodies, or veins and stringers in the igneous rocks. Some of the masive ores contain fragments of the host rock. The individual ore bodies are normally elongate, lenticular, or sheetlike and may extend for hundreds or thousands of feet.

Many deposits occur at or near the base of peridotite or norite intrusives and are particularly well formed in local hollows or reentrants along the basal contacts. Magmatic segregation is considered by many geologists to have been the mechanism by which these deposits were formed; immiscible liquid sulfide droplets were segregated from the parent mafic or ultramafic magma at an early stage of crystallization, settling downward and coalescing to form a sulfide zone at the base of the intrusive. The evidence in favor of this mechanism seems to be strongest in many small deposits associated with relatively small intrusives. For some larger deposits, although the mode of occurrence is similar, the origin is disputed; typical of these are the large deposits in the Sudbury district, Ontario, Canada, which occur along the base of a basin-shaped or funnellike norite intrusive. Hawley (1962) has recently summarized the case for origin of these deposits by magmatic segregation. Others (for example, Yates, 1948) support a theory of epigenetic origin—introduction of the sulfides into the norite contact zone by hydrothermal solutions that migrated from depth. Different theories of origin have

been proposed, and are summarized by Cornwall (1966).

Other nickel-bearing sulfide deposits occur along faults or shear zones; these are clearly epigenetic and the place of deposition was structurally controlled.

NICKELIFEROUS LATERITE DEPOSITS

Laterite has formed over large areas during long periods of intensive weathering and erosion, mainly in tropical to subtropical climates, where stable landmasses have gradually been reduced to almost flat featureless peneplains. Such a period of erosion took place during Tertiary time in many parts of the world. Where the rock exposed at the surface was peridotite (composed essentially of olivine and pyroxene), dunite (all olivine), pyroxenite (all pyroxene), or serpentinite (serpentinized peridotite), and laterite that was developed is almost invariably rich in iron and nickel.

The laterite formed from the weathering of serpentinite is richest in iron, generally containing 45–55 percent. The nickel content of this laterite commonly averages about 1 percent, ranging from about 0.9 to 1.3 percent for large volumes of material. These deposits are called nickeliferous iron laterite. The mode of occurrence of the nickel in this laterite is not known; most likely the nickel is included in the goethite, limonite, and serpentine minerals, which are the major constituents. Huge deposits of nickeliferous iron laterite, similar to those in Cuba, the Philippines, and Indonesia, are not known in North America, but several smaller deposits have been thoroughly explored in California, Oregon, and Washington.

The other type of nickeliferous laterite is known as the nickel-silicate type, because a significant part of the nickel occurs either as the hydrosilicate garnierite or as nickel-bearing talc or antigorite. This laterite has formed from the weathering of fresh peridotite, dunite, and, to a lesser degree, pyroxenite. The iron content is less than 30 percent in most laterite of this type; the SiO_2 content, which is very low in the iron laterite, may be as much as 30 percent; and the nickel content exceeds 1.5 percent and averages about 1.6 percent for large tonnages. The largest known deposits of nickel-silicate laterite occur in New Caledonia and Indonesia. A moderately large deposit occurs in the United States at Riddle, Oreg.

RESOURCES

IDENTIFIED RESOURCES

This discussion considers first the world sulfide resources and second the world laterite resources of nickel. The basic figures are given in tables 87 and 88 and are considered conservative. The United States resources are given by States; resources of other nations are listed by country.

The United States sulfide resources are quite large (6.9 billion tons) but low grade (0.21 percent Ni). The very large estimate of nickel in the Duluth Gabbro near Ely, Minn., is based on data recently released by the Minnesota Geological Survey (P. K. Sims, written commun., 1972). Canadian reserves of minable ore are the world's largest with probably close to 2 billion tons of material that can be mined under present economic conditions. Australia probably has great potential for increasing the present estimate of 400 million tons and the yearly production rate is growing rapidly. South Africa also has potential for greater than the 200 million tons estimated here. U.S.S.R. tonnage is probably greater than 100 million, but grade is probably less than 0.6 percent nickel.

TABLE 87.—*World nickel-sulfide identified resources*

[Identified resources are specific, identified mineral deposits that may or may not be evaluated as to extent and grade, and whose contained minerals may or may not be profitably recoverable with existing technology and economic conditions]

Area	Tons of ore	Ni (percent)
United States:		
California	100,000	1.5
Colorado	70,000	.8
Montana (Stillwater)[1]	150,000,000	.25
Missouri	10,000,000	.5
Nevada	30,000	.3
Pennsylvania (Gap)	800,000	.7
Washington	100,000	.9
Minnesota (Ely)[2]	6,500,000,000	.21
Alaska, Brady Glacier	200,000,000	.25
Yakobi Island	20,000,000	.3
Funter Bay	600,000	.35
Maine	10,000,000	1
Total (0.21 percent Ni avg)	6,900,000,000	
Canada:		
Thompson district:		
Thompson mine	150,000,000	3.0
Mystery Lake deposit	200,000,000	.45
Moak Lake deposit	400,000,000	.7
Others	250,000,000	1
Total (1.0 percent Ni avg)	1,000,000,000	
Sudbury district	400,000,000	1.5
Other Canadian	100,000,000	1.5
Other Canadian	200,000,000	.2
South Africa	200,000,000	1
Norway	2,000,000	1
Burma	25,000,000	.3
Australia	300,000,000	.6
Australia	100,000,000	1.5
U.S.S.R.	100,000,000	.6

[1] Also contains 0.25 percent Cu.
[2] Also contains 0.64 percent Cu.

TABLE 88.—*World nickel-laterite identified resources*

[Identified resources are specific, identified mineral deposits that may or may not be evaluated as to extent and grade, and whose contained minerals may or may not be profitably recoverable with existing technology and economic conditions]

Area	Tons of ore	Ni (percent)
Philippine Islands	1,000,000,000	0.8
Indonesia	500,000,000	.9
Australia	100,000,000	1.2
Solomon Islands	100,000,000	1.2
New Caledonia	500,000,000	1.8
Malagasy	2,000,000	2
Cuba	2,000,000,000	1
Dominican Republic	70,000,000	1.5
Guatemala	100,000,000	1.5
Venezuela (Loma Hierro)	60,000,000	1.6
Colombia (Cerro Matoso)	40,000,000	2.5
Brazil	20,000,000	2
Puerto Rico	100,000,000	.9
Greece	2,000,000	1.7
U.S.S.R.	100,000,000	1.5
Yugoslavia	20,000,000	1
United States:		
Nickel Mountain (Riddle), Oreg	10,000,000	1.5
Northern California and rest of Oregon	55,000,000	.75
Washington (Cle Elum, Blewett)	30,000,000	.5
North Carolina	5,000,000	1

The world nickel laterite resources (table 88) include areas that have only recently been explored, such as the Solomon Islands, Colombia, and Australia, but most of the remainder have been known for many years, particularly the larger resources. The United States laterite estimate of 100 million tons probably will not be greatly increased, and the individual laterite bodies that it comprises are small. A number of companies have been and are currently negotiating with local governments for operating concessions in the Philippines, Indonesia, New Caledonia, Colombia, and Venezuela, and development has been delayed by such negotiations and difficulties of financing in areas where the risk appears high.

In a few areas the laterite estimates are probably quite accurate; in others, when large-scale mining starts, renewed exploration probably will substantially increase the resource estimates, such as in Indonesia, Australia, and Colombia.

Another very large nickel resource, recently described by McKelvey and Wang (1969), occurs on the deep floor of the Pacfiic Ocean in the form of manganese-oxide nodules. The nodules cover 20–50 percent of the bottom in large areas of the northeast, central, and southern Pacific. In addition to dominant manganese and iron, the nodules contain copper, nickel, and cobalt, with an average ratio of 3:4:1. Nickel content ranges from 0.1 to 1.1 percent, but large deposits appear to contain 0.8–1.1 percent. Estimates of the size of the nodule deposits range from 90 billion to 1.7 trillion tons; thus for a liberal estimate, a resource of 1.7 trillion tons of nodules averaging 0.95 percent nickel would contain 16 billion tons of nickel. However, the amount in deposits of suitable quality, abundance, and environmental setting to warrant dredging is likely to be much smaller.

SPECULATIVE RESOURCES

The discovery of the Thompson district, Manitoba, in 1949, and particularly the discovery of the Thompson mine in 1956, revealed a new type of nickel-sulfide deposit. Data collected by the company geologists indicated that the nickel was derived from peridotite and serpentinite where metamorphosed to a garnet-amphibolite-sillimanite assemblage, indicating a temperature of 600°C or higher.

Unmetamorphosed peridotites in the area (as elsewhere in the world) contain 0.25–0.3 percent nickel; metamorphosed peridotite (metaperidotites) in the area contain significantly less. There is evidence that sulfur was available in hydrothermal solutions during metamorphism—metamorphosed iron-formation in the area has been partly converted to pyrrhotite ($Fe_{1-x}S$). In such an environment it is possible or even probable that nickel was mobolized by hydrothermal solutions during metamorphism and deposited at present sites as the sulfide (pentlandite), as first proposed by Michener (1957).

If this mechanism for the formation of the Thompson deposits is valid, peridotites throughout the world could have associated nickel-sulfide deposits where sufficiently metamorphosed in an environment where sulfur was available—for example, in proximity to black shales, which commonly contain sulfur in disseminated pyrite.

Another possibility that would make vast quantities of nickel available would be the development of new metallurgical techniques to produce nickel from peridotites and serpentinites. Large bodies of these rocks occur in certain areas of the world, including both Eastern and Western United States, and they universally contain 0.2–0.4 percent nickel. The nickel is probably included chiefly in the lattices of the silicate minerals (mainly olivine and serpentine), but no method is now available for extracting it economically.

As shown in table 87, conservative estimates of world nickel resources are about 2 billion tons of sulfide averaging 1.0 percent nickel and 7 billion tons averaging more than 0.2 percent nickel. For nickel laterites (table 88), the figure is about 5 billion tons averaging about 1.0 percent nickel. The

sulfide estimates might be doubled by new discoveries; the laterite estimate probably will not be as greatly expanded.

As mentioned above, if a practical method is found to extract the 0.2–0.4 percent of nickel universally disseminated through peridotites and serpentinites, vast amounts of nickel will become available. The total of estimates given in the preceding paragraph would be increased by several orders of magnitude. The potential size of nickel resources in unknown areas of deep-sea manganese nodules could be enormous.

PROSPECTING TECHNIQUES

Prospecting and exploration techniques are quite different for the sulfide-, laterite-, and nodule-types of nickel deposits. Prospecting for nickel sulfides can be well illustrated by briefly describing the methods used by Inco (International Nickel Co. of Canada, Ltd.) in their discovery of the major Thompson district in Manitoba in 1956. Geologists first studied aerial photos to find major structural lineaments and bodies of favorable rocks such as ultramafics with which nickel deposits are known to be associated. Such a lineament was discovered trending southwest from Hudson Bay through the Thompson area. The area was then flown with airborne magnetometer and electromagnetic equipment. Areas of coincidence of high magnetic anomalies and high electromagnetic conductivity were selected for exploration by diamond drilling. This drilling led to the discovery of two very large deposits of low-grade disseminated nickel sulfides in serpentinized peridotite intrusives. Attention was then turned to electromagnetic conductors that coincide with small magnetic anomalies. Such drilling resulted in the discovery of the Thompson deposit of nickel and iron sulfides in biotite schist that averages 3 percent nickel and extends for 3½ miles laterally and over 2,000 feet vertically.

Prospecting for nickel laterites involves first the identification of large laterite (intensely weathered saprolitic soils) areas overlying ultramafic rocks. Most of the large nickel or nickel-iron laterites have probably been found; they occur in or near the tropics and lie on Tertiary erosion surfaces. The first step in the search for such laterites is the delineation of old erosion surfaces in favorable areas. Then the areas of ultramafic rocks are outlined and the most promising selected for sampling on 500-foot or smaller centers. Sampling is done by augering or by digging pits. Nickel, iron, and magnesium determinations are made for 1- to 5-foot lengths in each hole. Thus areas of ore grade (commonly those of higher than 1 percent nickel) are delineated.

Nickel-bearing manganese nodules on the deep ocean floor are explored by dredging and bottom photography.

PROBLEMS FOR RESEARCH

Problems of developing potential nickel resources come under three headings: scientific, technological, and political.

Research on the origin of the metamorphosed ultramafic deposits (Thompson type) would almost certainly pay dividends in the form of new discoveries. How does the nickel occur in these peridotites, and what happens to it during metamorphism? What are the most favorable environmental factors for the formation of this type of deposit? What criteria can be used in searching for similar deposits elsewhere in the world?

The technological breakthrough of greatest potential value would be development of a technology for the extraction of nickel that is universally present in peridotites and serpentinites in small but abnormal amounts. For ocean-bottom manganese nodules, the cost and difficulty of recovery from mid-ocean depths of 3,500–4,500 meters are major problems. The separation and refinement of the nickel and other metals from the nodules also poses a metallurgical problem that has not yet been resolved.

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NIOBIUM (COLUMBIUM) AND TANTALUM

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ABSTRACT OF CONCLUSIONS

Niobium (columbium) and tantalum have become important metals in modern technology because of their metallurgical, electronic, chemical, and nuclear uses. Both metals occur in nature almost entirely as single isotopes Nb^{93} and Ta^{181} and are present in the earth's crust in estimated abundance of 20 ppm (parts per million) and 2 ppm respectively. Niobium and tantalum have strong geochemical coherence and occur together in most rocks and minerals; however, some rock types such as nepheline syenite and carbonatites contain niobium in great preponderance over tantalum. These elements occur in minerals chiefly as oxides and multiple oxides, hydroxides, a few silicates, and one borate; more than 90 mineral species are known.

Ore concentrations of niobium and tantalum occur in carbonatites and other rocks of alkalic complexes, certain types of granite, pegmatites, placers, and residual deposits. Most of the known deposits of niobium are found in carbonatites and those of tantalum are contained in pegmatites and placers. Most of the world's resources of niobium and tantalum lie outside the United States, and consequently these metals are almost entirely imported. Known resources within the United States could be utilized during times of national emergency but cannot at present compete with the larger and higher grade foreign deposits. On a worldwide basis, resources of niobium are more than adequate to supply the projected needs to the year 2000, but resources of tantalum barely meet these projected needs. Geologic research is needed to explore the possibilities of the existence of new types of tantalum deposits.

INTRODUCTION

Niobium (columbium) [1] and tantalum are two similar metals that have become increasingly important in modern technology because of physical properties that are useful in certain metallurgical, electronic, chemical, and nuclear applications. These metals were discovered in 1801–02, but for more than a century and a quarter no practical use was found for them. Commercial usage of niobium began about 1930 when it was first used as an alloying element in steel. Tantalum, although used to a minor degree in the chemical and electrical industries in the 1920's, was not extensively used until 1940 when it became an important material for capacitors. Both metals have been in strategically short supply at various times during and since World War II.

[1] Niobium (Nb) is the preferred name in chemistry and most other sciences and was officially adopted by the International Union of Pure and Applied Chemistry in 1950. The name columbium is still used to some extent in metallurgy and mineral trades.

Niobium is utilized chiefly in the form of ferrocolumbium as an alloying element in carbon and alloy steel, stainless steel, and superalloys. Of prominence in recent years has been the inclusion of niobium in high-strength low-alloy steels that are used in the construction of large buildings, pipelines, and machinery and structures where savings in weight and increased durability and strength are important factors. Niobium is added as a grain refiner and stabilizer in some stainless steels and variously improves the corrosion resistance, weldability, or formability of the material. Niobium is a common alloying addition to nickel-, iron-, or cobalt-based superalloys that have use in high-temperature and high-strength applications such as gas-turbine components and hot-gas ducting in aircraft. For example, niobium-based alloys are used in rocket engines and superconductors, and unalloyed niobium is used in currently classified nuclear applications, mainly in mill-product form.

More than half of the tantalum produced is used in the electronics industry, largely in the manufacture of capacitors and rectifiers. The remainder goes into the production of superalloys in high-temperature corrosion-resistant applications in aerospace vehicles, into tantalum carbide for high-temperature cutting tools, and into tantalum metal for a variety of corrosion-resistant usages such as prosthetic devices, chemical processing equipment, and liquid-metal containment apparatus.

Because niobium is principally used as a ferroalloy element in steel, its consumption is tied closely to the activities of the steel industry; a cutback in steel production is reflected in a low consumption of niobium. The consumption of tantalum is related chiefly to the level of production in the electronics industry.

In many applications vanadium can be substituted for niobium although some substitutions result in deficiencies in certain mechanical properties such as weldability in high-strength steel. Tantalum and titanium are possible substitutes for niobium in superalloys.

Aluminum and ceramic materials can be substituted for tantalum in capacitors, with corresponding tradeoffs among such things as durability, cost, and size of units. Molybdenum and tungsten are sometimes substituted for tantalum used in chemical environments, and they may be actually superior in some applications where halogens and halides are involved; however, unlike tantalum, both have poor weldability characteristics.

Except for material released from the government stockpile, the United States has imported all its niobium and tantalum since 1959. Some domestic deposits are known and have been variably explored, developed, or exploited, but none are commercially productive at the present time. These metals are imported mostly in the form of mineral concentrates chiefly from Brazil, Canada, and Nigeria and other African countries and in processed material in the form of ferrocolumbium from Brazil and of tantalum-bearing tin smelter slags from Malaysia.

EXPLOITATION

Limited demand for niobium and tantalum began in the first quarter of the 20th century and a low consumption continued until the World War II period at which time critical shortages of both niobium and tantalum developed (fig. 53). Tempo-

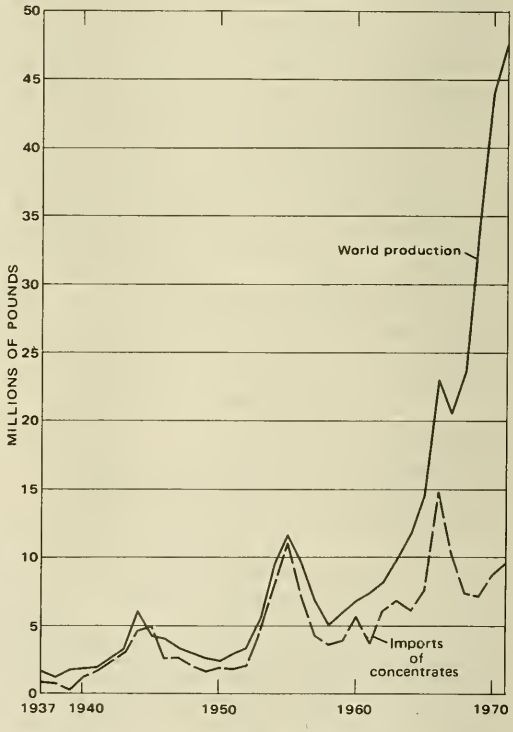

FIGURE 53.—World production and U.S. imports of niobium-tantalum concentrates, 1937–71. Data from U.S. Bureau Mines (1938–72). Note: Ferrocolumbium included in import data for 1964–68. Comparable data not available for 1970–71. One pound ferrocolumbium arbitrarily considered equivalent to 2 pounds niobium ore concentrate.

rary allocation controls were applied to the use of these metals, and some concentrates were airlifted to help alleviate the shortage which could not be met by domestic production. The increased need for these metals was caused by the increased use of niobium in high-temperature steel alloys and the use of tantalum as a catalyst in the manufacture of synthetic rubber.

A second period of critical shortage occurred in the early 1950's during the Korean conflict when niobium-bearing steel alloys were required in the greatly increased manufacturing of jet engines. At this time the United States instituted a guaranteed purchase program that promoted exploration, discovery, and production of niobium in both domestic and foreign deposits. The program resulted in the discovery of numerous large low-grade carbonatite deposits and some large placer deposits. One of these, the Bear Valley, Idaho, placer deposit, has been the site of the dominant and the only significantly large-volume niobium-tantalum production in the United States. This production ceased in 1959 because government purchase contracts were fulfilled at that time.

In the subsequent 10 years, production and consumption of niobium and tantalum generally followed the trend in production of steel which showed a general gradual increase, and niobium-tantalum consumption of the United States accounted for the largest proportion of the world production. However, during the last few years prior to 1972, as illustrated in figure 53, this relation has changed markedly, with the U.S. consumption of niobium, though increasing, greatly overshadowed by the much greater rate of increase in world production. The increased rate of world production is attributed to the rapidly expanding use of niobium in the manufacture of high-strength low-alloy steels by modern steel-manufacturing facilities in Japan and Western Europe.

ENVIRONMENTAL PROBLEMS

Mining operations for niobium and tantalum have no known unique features that affect the environment differently from the mining of many other ores. Open-pit mining of carbonatites presents the problems of large excavations and extensive waste disposal which in populated regions are offensive to view and may affect local property values. Placer mining and dredging of niobium-tantalum minerals requires the restoration of placered ground and also requires the application of measures to control the added mud and silt in the draining streams. Niobium-tantalum minerals themselves are not pollutants, and drainage waters from mines should not be degrading to the environment.

Niobium and tantalum are not hazardous metals; stack exhaust fumes, gases, and dust from extraction plants are easily controlled and offer no known health hazards or uncontrollable environmental problems.

GEOLOGIC ENVIRONMENT

GEOCHEMISTRY

Niobium is a chemical element with atomic number 41 and atomic weight 92.91; tantalum has atomic number 73 and atomic weight 180.95. In nature both elements consist almost entirely of single isotopes Nb^{93} and Ta^{181} (Strominger and others, 1958), with Ta^{180} accounting for only 0.01 percent of that element (Evans and others, 1955; White and others, 1955).

Niobium and tantalum have strong geochemical coherence; that is, they are closely associated and found together in most rocks and minerals in which they occur. Great preponderance of one element over the other rarely occurs in some rocks such as nepheline syenite (niobium-rich) or lithium-bearing pegmatites (tantalum-rich). The principal reasons for coherence are similar ionic radii and identical valence states (Nb^{+5} =0.69 A and Ta^{+5} =0.68 A). Both elements are lithophilic, showing strong affinity for oxygen and being enriched in the earth's crust (Rankama and Sahama, 1950). Niobium is also enriched in some carbonatites and kimberlites that are considered to be of mantle derivation.

The crustal abundance of niobium is considered by modern estimates to be about 20 ppm (parts per million) and of tantalum, to be about 2 ppm (summarized by Parker and Fleischer, 1968). The abundance is variable both in members of the same rock type in different localities and in different rock types. In general, however, lowest values of niobium and tantalum are found in some ultramafic rocks (not related to alkalic complexes) and some of the highest values of niobium are found in alkalic granites, nepheline syenites and related ultramafic rocks, pegmatites, and carbonatites. Highest contents of tantalum occur in albitized granites and pegmatites that are late-stage differentiates of granitic batholiths. Worthy of note is the fact that many carbonatite niobium deposits have very low contents of tantalum.

The small amounts of niobium and tantalum that are dispersed in ordinary magmatic rocks are chiefly present as "camouflaged" elements in iron- and iron-titanium-bearing minerals, to a certain extent in zirconium minerals, and rarely as discrete minerals

of niobium and tantalum. Where present in many rock-forming minerals, the niobium and tantalum are in limited substitution for titanium, tin, tungsten, and zirconium.

MINERALS

A glossary of niobium and tantalum minerals given by Parker and Fleischer (1968) shows that niobium and tantalum minerals are chiefly oxides, multiple oxides, and hydroxides, as well as a few silicates and one borate. More than 90 species are known; the most important ore minerals and their chemical compositions are listed below:

Columbite-tantalite ——— $(Fe,Mn)(Nb,Ta)_2O_6$
Euxenite ——— $(Y,Ca,Ce,U,Th)(Nb,Ti,Ta)_2O_6$
Fergusonite ——— $(Y,Er,Ce,Fe)(Nb,Ta,Ti)O_4$
Ixiolite ——— $(Ta,Nb,Sn,Fe,Mn)_4O_8$
Loparite (variety of perovskite) ——— $(Ce,Na,Ca)_2(Ti,Nb)_2O_6$
Microlite ——— $(Na,Ca)_2Ta_2(O,OH,F)_7$
Murmanite ——— $Na_2(Ti,Nb)_2Si_2O_6 \cdot nH_2O$
Pandaite ——— $(Ba,Sr)(Nb,Ti)(O,OH)_7$
Pyrochlore ——— $(Na,Ca)_2Nb_2(O,OH,F)_7$
Samarskite ——— $(Y,Er,Ce,U,Ca,Fe,Pb,Th)(Nb,Ta,Ti,Sn)_2O_6$
Wodginite ——— $(Ta,Nb,Sn,Mn,Fe)_{16}O_{32}$

TYPES OF DEPOSITS

Ore concentrations of niobium and tantalum occur in certain types of magmatic rocks and endogenic derivatives of those rocks. Commercial deposits have been found in various related rocks of alkalic complexes, such as nepheline syenites and carbonatites, certain granites, pegmatites, and placers. Some low-grade, widely disseminated, unexploited deposits of niobium occur in riebeckite granite and in bauxite derived from nepheline syenite.

ALKALIC ROCK COMPLEXES

NEPHELINE SYENITES

Nepheline-bearing syenites are among the types of rocks that may be greatly enriched in niobium and tantalum, particularly in their late phases such as pegmatites, albitized zones, and some carbonatites. Nepheline syenites are found in alkalic rock provinces throughout the world but are best known from their many occurrences in the U.S.S.R. where, according to Es'kova (1960), they constitute 1 percent of the exposed igneous rocks. In eight of the prominent nepheline syenite massifs of the U.S.S.R., the average niobium content ranges from 100 to 900 ppm, and the average tantalum content ranges from 12.0 to 20.5 ppm (Parker and Fleischer, 1968).

On the basis of chemical and mineralogical differences, there appear to be two distinct types of nepheline syenites, which have been given the distinguishing terms "agpaitic" and "miaskitic." As originally proposed by Ussing (1911), the agpaitic type is characterized by an excess of alkalies (K_2O+Na_2O) over alumina, in contrast to the "common" type in which this ratio is 1 or less. The agpaitic type is also characterized by the presence of complex zirconium- and chlorine-bearing minerals and sodic amphiboles and pyroxenes and by the general absence of calcite. Because of their enrichment in typical "rest elements" and in volatiles such as F, Cl, and H_2O, agpaitic nepheline syenites have a compositional resemblance to pegmatites (Sorensen, 1960). The "common" or miaskitic nepheline syenite, in addition to having the lower alkali-alumina ratio, differs from the agpaitic type in mineral assemblage by containing more of the common rock-forming species, such as biotite, augite, hornblende, sphene, and apatite, and fewer of the rare minerals of complex chemistry that are found in the agpaitic type. These and other characteristics of the two types, as well as some notable occurrences, are described by Heinrich (1966, p. 19).

Although both agpaitic and miaskitic syenites may be enriched in niobium and tantalum, they differ in the kind and number of minerals in which these elements occur. In agpaitic syenites and their derivatives, these two elements are largely fixed in titanium and zirconium minerals, many of which are rare species (Es'kova, 1960). In the miaskitic type, some of these minerals may be present, but there is a greater tendency for the formation of independent niobium-tantalum minerals such as pyrochlore, particularly in the late magmatic and postmagmatic derivatives.

Niobium- and tantalum-bearing agpaitic rocks make up much of the great Lovozero alkali massif in the Kola Peninsula, U.S.S.R., and have been described in detail by Vlasov, Kuz'menko, and Es'kova (1959). The massif as a whole contains about 900 ppm niobium and 70 ppm tantalum, but the content of these elements varies not only among the various differentiates but also within the layered rock units themselves, as for example, in porphyritic lujarvrite, which may contain 0.03–0.92 percent $(Nb,Ta)_2O_5$.

The principal niobium mineral in the Lovozero complex is loparite, a member of the perovskite group which contains about 12 percent $(Nb,Ta)_2O_5$. It is found to some extent in all the rocks of the complex but is most abundant where differentiation has been greatest, particularly in the base of urtite (nepheline-rich syenite) layers and the top of the underlying trachytic nepheline syenite. Niobium and tantalum are major constituents of several other

minerals of the complex in addition to loparite and are also present in minor amounts in many more.

Another important area of niobium mineralization is the Ilimaussaq complex in southwest Greenland where agpaitic nepheline syenites are overlain by lavas, gabbros, anorthosites, and augite syenite. All the rocks contain niobium minerals, chiefly pyrochlore and members of the epistolite-murmanite group, in shear zones and hydrothermal veins. The agpaitic rocks contain 500–1,500 ppm Nb_2O_5 and 15–60 ppm Ta_2O_5. The niobium content of the rocks of the complex increases from the preagpaitic rocks to the agpaitic rocks and further to the late hydrothermal veins (Hansen, 1968).

Alkalic complexes dominated by agpaitic rocks are found at various other places in the world, including the United States, but so far as is known, only those in the Kola Peninsula, U.S.S.R., have been economically exploited for niobium. Economic deposits are chiefly in the more numerous complexes of dominantly miaskitic rocks which are more favorable for the development of carbonatite bodies and veins. Although there are some exceptions (Sorensen, 1960), the miaskitic types are characterized by far less of the numerous zirconium-titanium minerals in which much of the niobium and tantalum in the agpaites is dispersed and are more apt to contain the niobium and tantalum in richer and more economically interesting species, notably pyrochlore, in minable concentrations in their related carbonatites.

Nepheline syenite bodies containing about 200 ppm niobium are the source rocks of the bauxite deposits of Pulaski and Saline Counties, Ark. Investigation of the trace-element content of the bauxite showed that a significant enrichment in niobium had taken place, the bauxite containing about 2.5 times the amount of niobium present in the parent rock (Gordon and Murata, 1952; Fleischer and others, 1952). Niobium in the syenite appears to be largely contained in accessory sphene which during bauxitization was altered to various other titanium minerals, chiefly ilmenite, which then became the principal carriers of niobium in the bauxite. The niobium enrichment parallels that of alumina, suggesting that the concentration was entirely residual.

CARBONATITES

Carbonatite bodies contain the most extensive known world resources of niobium. They commonly are found in the interior parts of alkalic intrusive complexes which contain a wide variety of rock types ranging from nepheline syenite to alkalic gabbro and pyroxenite. Many of these complexes are circular in plan (though some are not) and the constituting rocks including the carbonatites commonly are arranged in arcuate, radial, or irregular discordant masses within the complexes. Some carbonatites are found intruding unrelated country rocks, but most of the occurrences can be associated with nearby alkalic rocks.

Carbonatites and associated alkalic rocks range widely in age from Precambrian to Holocene and are not confined to any particular geologic period. Some complexes are linked to volcanic activity at the earth's surface, and actual carbonatite lavas are recorded at Oldoinyo Lengai in Tanzania (Tanganyika). Others not obviously related to any known extrusive rocks represent complexes exposed at deeper levels in the crust by a combination of erosion and geologic structure.

Carbonatites and related alkalic rock complexes are for the most part restricted to the stable parts of the continent. This distribution is true for Africa, South America, North America, and Eurasia. Some complexes tend to cluster along major crustal breaks such as the African rifts, whereas some show little relation to identifiable structures.

Carbonatites have been intensively explored over the world primarily in the search for niobium, and considerable information is now available on their nature and composition. Many carbonatites have been shown to contain deposits of one or more of the following metals or mineral commodities: Niobium, rare earths, copper, nickel, titanium, thorium, uranium, vermiculite, fluorite, zirconium, barite, apatite, and strontium. The carbonatite itself ranges from iron- and magnesium-bearing carbonates to nearly pure calcite, and some of this material is marketed for agricultural and other purposes. Some carbonatites conceivably could be exploited profitably for the collective recovery of more than one commodity, whereas on an individual basis the commodities might be marginal or submarginal economically.

Explored niobium deposits in carbonatites contain immense reserves of niobium. The grades range from below 0.2 percent Nb_2O_5 to more than several percent. Some of the largest deposits exceed 8 million tons of Nb_2O_5 which occurs in the carbonatites chiefly as the mineral pyrochlore.

Some representative niobium-bearing carbonatites in various parts of the world are listed below:

Iron Hill, Colo. ---------- Temple and Grogan (1965).
Gem Park, Colo. ---------- Parker and Sharp (1970).
Oka, Quebec ---------- Gold (1966).
Axárá, Brazil ---------- de Souza and Castro (1968).
Fen, Norway ---------- Saether (1957).

Lueshe, Congo ---------- Wambeke (1965).
Sukulu, Uganda ---------- Davies (1956).
Kaiserstühl, Germany -------- Wambeke and others (1964).

Although some disagreement exists on the origin of carbonatites, prevailing opinion is that they are intimately related to alkalic rocks including kimberlites and that they probably originated from material derived at great depth, possibly within the mantle (Heinrich, 1966).

GRANITIC ROCKS

Niobium and tantalum are present in most granitic rocks in trace amounts in iron- and iron-titanium-bearing minerals and to some extent in zirconium minerals. A few rare granites contain columbite, euxenite, fergusonite, or pyrochlore as accessory minerals to the extent that economic concentrations of these minerals may develop through the weathering of the rocks either in residual deposits or in placers.

The Jos Plateau in central Nigeria is an important producer of columbite which is obtained in part from alluvial and eluvial concentrations from Precambrian pegmatites, but mainly from alluvial deposits and saprolite derived from biotite granites. These granites are part of an igneous complex of possible Jurassic age (Black and Girod, 1970) known as the Jos-Bokuru Younger Granite complex which occupies an area of more than 100 square miles. The complex includes gabbros, porphyries, rhyolites, biotite granite bodies, and riebeckite granite (Mackay and others, 1949). Several phases of the biotite granite, all of which contain accessory columbite, have been recognized. The Rayfield-Gona and Forum phases are the richest and contain an average of 0.4 pound columbite per ton, and as much as several pounds per ton are found in local concentrations (Williams and others, 1956). Columbite is also an accessory mineral in the Lunyo albite granite in Uganda (Knorring, 1960). Other accessory minerals in this rock include magnetite, cassiterite, zircon, thorogummite, fluorite, and pyrite. Columbite granites may not result entirely from magmatic processes but may involve autometasomatic processes resembling greisenization in which calcium is removed from plagioclase and iron, titanium, niobium, and tantalum are removed from biotite. These elements are recombined to form fluorite, magnetite, and columbite (Parker and Fleischer, 1968).

Euxenite-bearing granitic rocks (quartz monzonite or quartz diorite) in the Idaho batholith contain from a trace to 0.05 pound of euxenite per cubic yard and with their related pegmatites are the apparent source of the euxenite placer deposits in Bear Valley, Idaho (Mackin and Schmidt, 1956). A fergusonite granodiorite in the Nang-ling Range in southern mainland China has been described by Wang (1964). From the English summary of Wang's report (Lee, 1970, p. 22), the fergusonite is most abundant in the marginal zone of the granodiorite. Fergusonite granite has also been found in the basin of the Gava Say River in the U.S.S.R. (Parker and Fleischer, 1968).

Pyrochlore granites are highly alkalic rocks composed principally of microperthite, sodic plagioclase, quartz, sodic amphibole, and sodic pyroxene. Pyrochlore is present in the Mount Rosa Granite, a riebeckite granite in the Pikes Peak area, Colorado (Gross and Heinrich, 1965), and in a riebeckite granite phase of the Jos-Bokuru complex in Nigeria. The pyrochlore content of the Nigerian granite from one occurrence was estimated to be about 0.7 percent (Mackay and others, 1949, p. 79).

PEGMATITES

Pegmatites are a type of igneous rock generally considered to represent the crystalline product of residual magmatic fluids and as such may contain concentrations of a number of rare elements whose properties inhibited their entry into minerals of earlier formed rocks. Pegmatites are commonly of granitic composition, but pegmatitic phases of other rocks, such as syenites, are found in some districts. A characteristic of pegmatites is the large but extremely variable grain size of the constituent minerals. Some pegmatites contain roughly concentric layers or zones of contrasting mineral assemblages, while others are unzoned with an essentially random distribution of minerals.

Pegmatites were for many years the major source of niobium and tantalum, and whereas niobium is now obtained largely from carbonatites, pegmatites still remain the dominant primary source of tantalum. These elements may be present in pegmatites, either in one or more of a large number of independent minerals of which columbite-tantalite is the most common or in the structure of such carrier minerals as micas, garnets, tourmaline, ilmenite, or zircon. Certain types of pegmatites seem to be more intensely mineralized with niobium and tantalum than others. These are commonly the complexly zoned pegmatites characterized by abundant albite and a strong development of lithium and beryllium minerals.

The tendency for pegmatite minerals to occur in large crystals and to be localized in distinct zones has favored the recovery of niobium-tantalum minerals from deposits that would otherwise be unminable. Pegmatites in tropical areas may also be deeply

weathered, so that some of the heavy resistate minerals may be recovered from the saprolite by simple placer-type methods.

Columbite-tantalite and other niobium-tantalum minerals occur in pegmatites throughout the world, but only a few deposits have been sufficiently rich to be mined solely for these minerals, and they are more commonly a coproduct or byproduct of mica, beryl, or cassiterite operations. In the United States, intermittent recovery of niobium-tantalum minerals, chiefly columbite, has been made from almost all areas where pegmatites are found (Barton, 1962). The Harding pegmatite, in Taos County, N. Mex., was an important source of tantalum during World War II and supplied about 3 tons of microlite concentrates during a brief period when tantalum was in very short supply (Montgomery, 1947). By 1946, about 17,200 pounds of microlite had been produced from the deposit (Berliner, 1949). The unusual concentration of tantalum in the pegmatite is thought by Montgomery (1950) to have been derived from a genetically related granite in which tantalum is largely concentrated in sphene.

The present major source of tantalum in North America is a pegmatite, the Bernic Lake deposit in southeastern Manitoba, that has been estimated to contain about 2 million tons of ore containing 0.23 percent Ta_2O_5 (Howe, 1968). Like the Harding pegmatite, it is a complexly zoned deposit containing lithium and beryllium as well as tantalum and niobium. The principal ore mineral at Bernic Lake is the uncommon mineral wodginite which occurs mainly in a potassium feldspar-muscovite-quartz-beryl zone lying below the quartz core (Grice and others, 1971).

PLACER DEPOSITS

Concentrations of niobium and tantalum minerals in various types of placer and residual deposits have been significant sources of these elements. Individual deposits of these types commonly are small but may be sufficiently numerous in a local area to constitute an economically important district.

Resistate heavy minerals such as columbite or tantalite, when released from their host rock by weathering, may accumulate essentially in place and become enriched in the rock debris by chemical and mechanical removal of other less durable and lighter weight minerals. Such accumulations in eluvium may constitute economic deposits minable by placer methods.

Transport and redeposition by running water can form concentrations of niobium and tantalum minerals in alluvial placers, the richest being in or near the source area at some site where the velocity of the water is reduced to the point where the heavy-mineral grains can no longer be transported. This reduction of velocity can result from many factors largely related to the geomorphic history of the terrain.

Heavy-mineral concentrations formed along sea beaches by wave action are important sources of monazite, zircon, and rutile. Niobium and tantalum minerals, however, are rarely reported from these placers, but it is quite probably that unsuspected niobium enrichment either from independent niobium minerals or from carrier minerals would be found by analytical studies of sea-beach concentrates.

Consolidated equivalents of sea-beach placers are found in sedimentary rocks; notable are those of Cretaceous age in Wyoming and other western States. Some of these fossil placers are large enough to constitute possible future sources of titanium, zirconium, and rare earths. A niobium-bearing opaque radioactive mineral found in the Wyoming deposits and tentatively identified as euxenite could be a coproduct of these placers if they were exploited (Houston and Murphy, 1962).

The most important placer deposit of niobium and tantalum known in the United States is at Bear Valley, Valley County, Idaho. The placer was mined from 1955 through 1959 by two dredges with a combined capacity of 8,000 cubic yards per day, and during the period of operation 1,050,000 pounds of combined niobium and tantalum oxide was produced from the euxenite and subordinate columbite recovered from the deposit (Barton, 1962). It has been estimated that there is sufficient unmined ground to permit 30 years' mining at the same rate of operation (Mining World, 1958).

The placer area is in a glaciated valley in the granitic rocks of the Idaho batholith; the richest placers, which have been partially mined, are in the upper part of the valley where the source of the valuable minerals is thought to be a 6-square-mile area of quartz diorite and associated pegmatites (Mackin and Schmidt, 1956). The euxenite content of the quartz diorite is very irregular and may range from a trace to 0.05 pound per cubic yard; this has been enriched to about 1 pound per cubic yard in the placers, where the euxenite is accompanied by a large suite of other heavy minerals, some of which, with their estimated tenor in pounds per cubic yard, are as follows: Columbite (0.2), ilmenite (20), magnetite (5), zircon (0.05), garnet (5), and monazite (0.5).

During the processing of the placer sands, euxen-

ite, columbite, and monazite were the principal products, and ilmenite, magnetite, zircon, and garnet were the stockpiled byproducts (Dayton, 1958).

The euxenite placers of Bear Valley are thought to be the result of a fortuitous combination of the following factors: (1) Local concentrations of the mineral in the quartz diorite and pegmatites, (2) sufficient disintegration of the host rock to free the minerals, (3) the action of Pleistocene glaciers which dammed the local drainage and led to the accumulation of valley fill, and (4) quickened downslope movement of enriched mantle during the periods of glaciation (Mackin and Schmidt, 1956).

Other placer deposits in Idaho, particularly the Dismal Swamp deposit in Elmore County, contain niobium and tantalum minerals (Armstrong, 1957; Savage, 1961), but none of these are known to be comparable in size or grade to those at Bear Valley.

RESOURCES

IDENTIFIED RESOURCES

The most extensive resources of niobium and tantalum (tables 89, 90, and 91) are found in Brazil, Canada, and several African countries. Known re-

TABLE 89.—*Reserves of niobium and tantalum*

[Reserves: Identified deposits from which minerals can be extracted profitably with existing technology and under present economic conditions]

Locality	Ore (tons)	Grade (percent)	Nb_2O_5 content (tons)	Ta_2O_5 content (tons)	Type of deposit
North America					
Canada:					
Lake Nippissing, Ontario	5,000,000	0.7	35,000	-----	Carbonatite.
Lakner Lake, Ontario	50,000,000	.26	130,000	-----	Do.
Chapleau, Ontario	20,000,000	.5	100,000	-----	Do.
	15,000,000	.3	45,000	-----	
James Bay, Ontario	40,000,000	.52	208,000	-----	Do.
St. Honoré, Quebec	100,000,000	.5	500,000	-----	Do.
Oka, Quebec	225,000,000	.35	787,500	-----	Do.
Bernic Lake, Manitoba	1,900,000	.23	--------	4,370	Pegmatite.
Bugaboo Creek, British Columbia	(1)	(2)	5,100	-----	Placer.
Total	----------	---	1,810,600	4,370	
United States:					
Iron Hill, Colo.	40,000,000	.25	100,000	-----	Carbonatite.
Bear Valley, Idaho	(3)	(4)	8,000	2,000	Placer.
Harding mine, N. Mex.	100,000	.1	--------	100	Pegmatite.
Total	----------	---	108,000	2,100	
South America					
Brazil:					
Araxá	300,000,000	3.0	9,000,000	-----	Carbonatite.
Tapira	10,000,000	.5	50,000	-----	Do.
Tantalite deposits	----------	---	--------	4,000	Pegmatite.
Total	----------	---	9,050,000	4,000	
Other:					
French Guiana (tantalite)	300,000	.4	--------	1,200	Do.
Guyana (tantalite)	----------	---	500	250	Do.
Total	----------	---	500	1,450	
Europe					
Germany: Kaiserstuhl	750,000	0.5	3,750	-----	Carbonatite.
Norway: Søve	61,000,000	0.2–0.5	138,500	-----	Do.
Total	----------	---	142,250	-----	
Africa					
Congo:					
Lueshe	30,000,000	1.34	402,000	-----	Do.
Bingo	7,100,000	2.4–3.6	198,000	-----	Do.
Columbite-tantalite	----------	---	50,000	50,000	Pegmatite-placer.
Kenya: Mrima Hill	56,000,000	.67	375,200	-----	Carbonatite.
	50,000,000	.7	350,000	-----	
Nigeria:					
Kaffo Valley	140,000,000	.26	364,000	-----	Granite.
Jos Plateau	----------	---	100,000	10,000	Placer.
Uganda: Sukulu	200,000,000	.25	500,000	-----	Carbonatite.
Malawi: Ilomba	100,000	.33	300	-----	Pyroxenite.
Total	----------	---	2,744,500	60,000	

[1] 65 million cu yd. [2] 0.1 lb per cu yd. [3] 200,000,000 cu yd. [4] Estimated euxenite content, 1 lb per cu yd.

TABLE 90.—*Conditional resources of niobium and tantalum*

[Conditional resources: Specific, identified mineral deposits whose contained minerals are not profitably recoverable with existing technology and economic conditions]

Locality	Type of deposit	Ore (tons)	Grade (percent)	Nb_2O_5 content (tons)	Ta_2O_5 content (tons)
North America (United States):					
Bauxite deposits, Arkansas	Byproduct potential.	54,000,000	0.05–0.15	55,100	
Magnet Cove, Ark	Carbonatite	12,000,000	.08	10,000	
Africa:					
Nigeria: Jos Plateau		[1]			
Malawi: Chilwa Island	Residual material.	Several million	.21		
Other:[2] South America, Africa, Asia, and Europe.				Several-thousand	Several-thousand

[1] Several hundred million tons of ore is inferred.
[2] Tin smelter slags; based on estimated 1970 production times 10; exclusive of U.S.S.R.

TABLE 91.—*Unevaluated resources of niobium and tantalum*

Locality	Type of deposit
North America (United States):	
Gem Park, Colo	Carbonatite.
Potash Sulfur Springs, Ark	Do.
Rocky Boy, Mont	Do.
Europe:	
Finland: Sokli	Do.
Portugal (tin-tantalite)	Pegmatite and placers.
Africa:	
Tanzania: Oldonyo Dili	Carbonatite.
North Rhodesia:	
Feira District	Do.
Nkumbwa Hill	Do.
South Rhodesia:	
Bikita	Pegmatites.
Darowa	Carbonatite.
Gabon: Columbite-tantalite	Pegmatites.
South West Africa:	
Orange River area	Do.
Karabib-Omaruru area	Do.
Zambia:	
Nkombwa	Carbonatite.
Kaluwe	Do.
Malagasy Republic	Pegmatite.
Mozambique	Do.
Republic of South Africa: Glenover	Carbonatite.
Asia:	
Malaya	Pegmatites and placers.
Thailand: Phang Ngo	Placer.
India: Ambadongar	Carbonatite.
Australia: Western Australia	Pegmatites and placers.

sources of these elements in the United States are relatively small. The United States as a major consumer of these elements must therefore look to these foreign sources for its present and near-future supply.

In the past, small amounts of niobium and tantalum were produced from the numerous pegmatite districts in the United States, commonly as byproducts of mining for mica, beryl, and lithium minerals. This small and erratic source of niobium and tantalum is rather insignificant when compared to the large pyrochlore deposits now supplying most of the niobium markets.

The most significant resources of niobium in the United States are contained in carbonatites at Iron Hill and Gem Park, Colo.; Rocky Boy, Mont.; and Magnet Cove and Potash Sulfur Springs, Ark.; in euxenite placer deposits at Bear Valley, Idaho; and in the bauxite deposits of Arkansas. Minor tantalum resources are also contained in the placer deposits of Bear Valley, Idaho, and in pegmatites widely distributed in the United States but especially at the Harding mine, N. Mex.

Three of the carbonatites are not sufficiently explored to be included in the computation of reserves, and one (Magnet Cove) is of lower grade than that of deposits now considered minable. The Arkansas bauxite deposits contain 0.05–0.15 percent Nb_2O_5 and constitute a major potential resource, but recovery of the niobium, although it can be made during the processing of the bauxite, is unprofitable under present market conditions.

At least half of the evaluated domestic deposits, therefore, are of much lower grade than those considered as commercial sources and must be classed as resources rather than reserves. Such deposits, however, remain strategically important and could be utilized in times of national emergency.

Distinction between world deposits that constitute reserves and those that are conditional resources cannot be made on a strict tonnage and grade basis. Deposits shown as reserves (table 89) include some which are now being mined as well as others which would appear to be minable but which are not now competitive with the larger and richer deposits. The resources shown in table 90 are largely carbonatites that are known to contain niobium minerals but are otherwise unevaluated. Also listed in table 90 are some evaluated deposits of grade of 0.2 percent or below, which are considered subeconomic at the present time.

The identified resources of niobium and tantalum of the world (exclusive of U.S.S.R. and Iron Curtain countries) are summarized in table 92.

TABLE 92.—*Summary of identified resources of niobium and tantalum in the world*

[Identified resources: Specific, identified mineral deposits that may or may not be evaluated as to extent and grade, and whose contained minerals may or may not be profitably recoverable with existing technology and economic conditions]

	Nb_2O_5 content (tons)	Ta_2O_5 content (tons)
Reserves[1] (see table 89):		
North America	1,918,600	6,470
South America	9,050,500	5,450
Europe	142,250	------
Africa	2,744,500	60,000
Total reserves	13,855,850	71,920
Total reserves rounded	14,000,000	72,000
Total conditional[2] resources (see text)	14,000,000	72,000
Total identified resources	28,000,000	144,000

[1] Reserves: Identified deposits from which minerals can be extracted profitably with existing technology and under present economic conditions.

[2] Conditional resources: Specific, identified mineral deposits whose contained minerals are not profitably recoverable with existing technology and economic conditions.

About 14 million tons can be identified as a minimal figure for reserves of Nb_2O_5 in deposits in the world, and similarly a figure of 73,000 tons is minimal for reserves of Ta_2O_5. Additional resources of probable lower grade exist at many of the explored deposits as unevaluated protore bedrock beneath some surficial weathered deposits in some carbonatite complexes and in some weathered pegmatite and granite deposits. Some deposits also contain lower grade material that was not included in reserve calculations because it was below the grade of material being considered at the time of evaluation, and some deposits have been identified as containing niobium and tantalum minerals but have not been sufficiently explored or evaluated. These materials in these deposits all constitute conditional resources. The distribution and extent of known low-grade or unevaluated deposits suggest that such conditional resources are at least equal to the computed reserves or 14,000,000 tons Nb_2O_5 and 70,000 tons Ta_2O_5.

UNDISCOVERED RESOURCES

Undiscovered resources no doubt occur as blind ore bodies in known carbonatites or as ore bodies in undiscovered carbonatites in known carbonatite provinces. These hypothetical resources will continue to be discovered through continuing geologic and exploration activities and constitute probably several times the amount of currently known resources.

Some undiscovered resources termed speculative resources might lie in undiscovered carbonatite provinces or in new geochemical and geologic environments for these elements. For example, until the post-World War II era, commercial niobium deposits were considered to be restricted to pegmatites and related placers; the discovery of low-grade large-tonnage carbonatite-pyrochlore deposits, however, changed the whole resource picture for niobium.

One might speculate that such a low-grade large-tonnage type of source lies undiscovered for tantalum and that additional new types of sources exist for niobium. Conceivably, unknown fossil placers exist that are large low-grade resources. Discoveries of such resources will depend on future scientific and technological advancements in exploration and geologic knowledge in order to discover the deposits that lie beneath great areas of volcanics, younger sedimentary rocks, and unconsolidated materials.

PROSPECTING TECHNIQUES

Inasmuch as alkalic-rock complexes and associated carbonatites at the present time are the chief targets for large low-grade niobium deposits, their recognition is the first step in exploration. Recognition has been made in the process of geologic mapping, through aerial observation and photography, and through geophysical surveying. The common circular plan and concentric arrangement of rocks constituting alkalic complexes can be distinguished and rock types can be identified by the usual geologic-mapping techniques, and these discordant structures are sometimes evident on aerial photographs in areas of surface exposure.

Where these structures are covered with overburden or younger rocks, their magnetite content can be a factor in their detection. Both airborne and ground magnetic surveys have been employed to successfully detect magnetic anomalies, some of which have been shown to be caused by carbonatite niobium deposits. The natural association of niobium with uranium and thorium makes radiation detectors a useful exploration tool. Many occurrences of niobium have been found with the aid of these detectors, and new improved airborne radiometric detectors have great potential for prospecting. Seismic surveying and gravity measuring techniques have proved useful where information on depth of overburden or information on differences in rock densities was desired. Future prospecting methods no doubt will employ combinations of these techniques, both airborne and on the surface, to outline the basic targets for exploration.

Once the target is identified, it must be evaluated by conventional exploration procedures. Niobium and tantalum minerals are not easily identified, and niobium and tantalum are not easily detected with-

out special means because of their insolubility in most solutions and their refractory nature. Qualitative and quantitative chemical determinative procedures have been developed for niobium and have been used in the field. Such chemical procedures have not been satisfactorily developed to conveniently detect tantalum. The capacity to analyze large numbers of samples at the site has been demonstrated by Grimes and Marranzino (1968), utilizing truck-mounted spectrographic equipment, and this method has been effective for rapid determination of niobium. Similar rapid analyses for both niobium and tantalum can be accomplished in the laboratory by X-ray fluorescence spectroscopy.

PROBLEMS FOR RESEARCH

One of the basic problems relating to niobium and tantalum is the lack of domestic selfsufficiency in resources of these elements in the United States. The United States is the world's largest single consumer, but these commodities are almost entirely imported. On a worldwide basis, supplies of niobium are more than adequate for projected needs to the year 2000 (Griffith, 1970) with chief sources in Brazil, Canada, and the African continent.

Tantalum resources also are very limited in the United States, and ores are wholly imported from Brazil, Canada, and certain African countries. Even on a worldwide basis, the known resources of tantalum are not large, and this fact has served to limit industrial use of the metal and to discourage research on new applications. Pegmatites and placers are the only known commercial sources of this metal, and low-grade large-tonnage commercial deposits have yet to be discovered.

Geologic research is needed to explore the possibilities of the existence of additional types of tantalum deposits. Such research has been hampered in the past by the lack of accurate abundance and analytical data on tantalum that in turn is a result of the lack of availability of sufficiently sensitive analytical techniques. Only neutron-activation analysis and elaborate chemical analysis currently are capable of detecting tantalum at the low values at which it is present in ordinary rocks. Research in new analytical techniques should receive first priority in any research effort directed toward discovery of additional resources of tantalum.

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NUCLEAR FUELS

By Warren I. Finch, Arthur P. Butler, Jr., Frank C. Armstrong, Albert E. Weissenborn, Mortimer H. Staatz, and Jerry C. Olson

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INTRODUCTION

By Warren I. Finch

The increasing demand for energy throughout the world and the decreasing resources of organic fuels place the nuclear fuels, uranium and thorium, in the spotlight of future energy sources. Technologically, uranium's role is well established, but thorium's future use as a fuel is less certain.

Thorium is about three times more abundant in the earth's crust than uranium. In igneous rocks the two elements are closely associated with each other; in the sedimentary cycle, however, they mostly part ways. The primary thorium minerals are resistant to oxidation, and weather out to form economically important placers. Thorium does not tend to enter the regimen of ground and meteoric water, rarely forms secondary minerals, and thus occurs in far fewer geologic environments than uranium. The primary uranium minerals, except those in which uranium substitutes for thorium, are easily oxidized. The most important placer concentrations of primary uranium minerals are those that are believed to have formed under nearly oxygen-free reducing atmos-

pheric conditions in early Precambrian time. Uranium is very mobile in ground and meteoric water systems and reconstitutes into deposits in many kinds of rocks and environments. Uranium forms a great variety of minerals, many of which form rich concentrations, of higher grade than thorium, that are economically attractive. The ultimate resource of thorium, however, is greater than that of uranium.

URANIUM

By Warren I. Finch, Arthur P. Butler, Jr., Frank C. Armstrong, and Albert E. Weissenborn

ABSTRACT OF CONCLUSIONS

Uranium is an important energy resource, and even though the demand for its use in nuclear-powered electrical generators was only moderate in 1972, near-future needs are expected to be very great. In the United States, large exploitable deposits are found chiefly in sandstone and associated rocks. In other parts of the world, large deposits are mainly in quartz-pebble conglomerate of early Precambrian age and in veins. Domestic resources recoverable at present prices totaled about 273,000 tons of U_3O_8 at the end of 1971, and the total for all countries reporting resources is about 1.6 million tons of U_3O_8. These supplies are sufficient to last into the 1980's. Needs beyond 1980 are so great that tremendous efforts in exploration, and research in ore-finding techniques, will be required to discover new recoverable resources. Identified low-grade paramarginal and submarginal resources in marine phosphorite and black shales and in igneous rocks are very large, but to obtain significant supplies of uranium from these sources would require mining and treating vast quantities of rock, disrupting large areas of ground at high unit costs.

INTRODUCTION

Uranium is a silvery white metal that consists of the three semistable radioactive isotopes U^{238}, U^{235}, and U^{234}. It is an important energy source because fission of isotope U^{235} releases large amounts of energy. This readily fissionable nuclide constitutes only about 0.7 percent of natural uranium. The isotope U^{238} makes up most of the remaining 99.3 percent and the third, U^{234}, only about 0.005 percent. U^{238} is not readily fissionable, but it is fertile material that under neutron bombardment converts to plutonium-239, which is fissionable.

Prior to 1942, uranium was used chiefly for coloring glass and ceramic glazes. An ample supply was obtained by recovering some uranium from ores mined at first for radium and later for vanadium. In 1942, controlled nuclear fission was demonstrated, and uranium had two new and vastly more important uses: as an explosive by the military and as a source of heat to produce steam for generating electricity. With continued development of nuclear reactors to generate electricity, uranium is destined to become one of the principal energy sources for the world, for even "in today's light water reactors without plutonium recycle, in which less than one percent of the total potential heat content is made available, a pound of U_3O_8 produces the heat equivalent of about eight tons of coal" (Johnson, 1972).

Military uses for explosives stimulated search for uranium that by 1956 yielded a surplus of that element. In the 1960's, nuclear reactors for generating electricity were developed from the experimental stage to the commercial stage. By December 1971, domestic nuclear-powered electric plant capacity was about 10 million kw (kilowatts) (nearly 3 percent of the total U.S. electric utility capacity of 357 million kw); about 45.8 million kw capacity was being built, and about 51.6 million kw was ordered (U.S. Atomic Energy Commission, 1972a). The domestic electric power need is growing at a rate of 7–8 percent per year, and the nuclear share is expected to grow at a faster and increasing rate, so it is predicted that in the year 2000 nuclear plants will provide about 60 percent of the total electrical power (U.S. Department Interior, 1972).

Although the demand for electricity generated by nuclear energy is expected to increase significantly for many years, technological developments may ultimately permit a decrease in the amount of uranium required to generate the needed electricity. If fast-breeder reactors are developed by the mid-1980's, annual domestic uranium requirements are expected to peak about 1990 at about 100,000 short tons of U_3O_8, about 10 times the 1972 requirement (solid line, fig. 54), after which they will decline gradually to about the same level as in 1972 as the currently used nonbreeder reactors are phased out

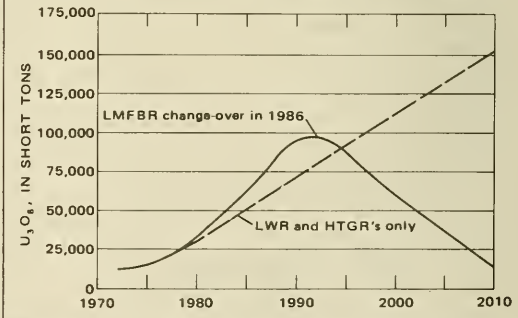

Figure 54.—Projected domestic annual uranium requirements, 1972–2010, using light-water reactors (LWR) and high-temperature gas-cooled reactors (HTGR) only, relative to changeover to fast-breeder reactors (LMFBR) in 1986 (Johnson, 1972).

owing to obsolescence. If, on the other hand, fast-breeder reactors are not successfully developed, uranium requirements will continue to increase, as shown by the dashed line on figure 54.

The identified domestic recoverable resources of 273,000 short tons U_3O_8 as of December 31, 1971, can supply domestic requirements into the early 1980's. After that time, uranium requirements probably cannot be satisfied merely by finding new ore bodies in the known mining districts, but will require the discovery of new districts. This task poses a great challenge to industry. Guides to new districts are urgently needed.

The world nuclear electric capacity was about 18,000 MWE (megawatts electrical) in January 1969 and is expected to grow to between 230,000 and 330,000 MWE by 1980, according to the European Nuclear Energy Agency and International Atomic Energy Agency (1969, p. 19). Total cumulative world uranium demand for the period 1970–80 is estimated at 563,000–739,000 short tons of U_3O_8, and world demand of 73,000–106,000 short tons is anticipated in 1980.

Thermal and nuclide pollution from nuclear reactors are serious problems that challenge technical ingenuity and affect the cost of nuclear electric power. The half-lives of some nuclides require safe disposal or storage for 10,000–500,000 years.

EXPLOITATION

Uranium was discovered in 1789 by Marten Klaproth in pitchblende from a mine in Germany. The element was first isolated in 1842. Radioactivity was discovered in 1896, and radium, a daughter of uranium decay, was discovered by the Curies and Bemont in 1898 in pitchblende from Joachymov (Joachimsthal), Czechoslovakia, where the mineral had been known since 1727. In the early 1900's, radium became important in medical therapy. This led to the search for uranium ore as a source for radium. The first important sources of radium outside Czechoslovakia were the uranium-vanadium sandstone deposits in western Colorado and eastern Utah from which about 275,000 tons of ore was produced during the period 1898–1923. This ore yielded about 200 grams of radium, 2,000 tons of vanadium, and a small but indeterminate amount of uranium; most of the uranium went into the tailings (Fischer, 1968).

In 1923, the U.S. deposits were supplanted as the source of radium by the large and rich Shinkolobwe vein deposit in the Belgian Congo. In 1933, production began from another vein deposit, the Eldorado at Port Radium, Northwest Territories, Canada, and thereafter the market was shared by Canada and the Belgian Congo. Only minor amounts of domestic uranium-vanadium sandstone ore were mined from 1924–1935.

In 1936, mining of the uranium-vanadium ores increased markedly owing to increased demand for vanadium. In anticipation of the development of controlled nuclear fission, the United States in 1940 began to recover uranium from tailings discarded during radium and vanadium operations, and by the end of 1947 a total of 1,440 tons of U_3O_8 had been produced (U.S. Atomic Energy Commission, 1959). In addition, the United States procured about 10,150 tons of U_3O_8 from outside sources, mainly Canada and the Belgian Congo. Prior to 1940, the total production from all world sources was slightly more than 7,500 tons of U_3O_8.

To meet military needs, the U.S. Atomic Energy Commission established in 1948 a domestic minimum price schedule that included bonus payments for discovery and production of high-grade ore. The base price was raised in 1951. These incentives brought about the first large-scale mining of uranium-vanadium ores solely for uranium, and led to the discovery of many large deposits not only in the Colorado Plateau region, but also in Washington, Wyoming, South Dakota, and Texas. By 1956 it was clear that the newly discovered domestic and foreign resources of uranium were adequate for military needs as well as for its experimental use in nuclear reactors for producing electricity. Accordingly, the U.S. Atomic Energy Commission announced in 1956 that after March 31, 1962, a price of $8 per pound for U_3O_8 concentrate would replace the original price schedules. Later they announced that ore discovered after November 24, 1958, would not be purchased under any of the existing price schedules, and that if it were purchased at all, each sale would be individually negotiated. In 1959, the U.S. Atomic Energy Commission relinquished its options to continue foreign purchases and in 1962, proposed to stretch out domestic purchases.

Annual domestic production reached a maximum of 18,800 tons of U_3O_8 in 1960, whereas world production peaked at more than 44,000 tons in 1959 (fig. 55). Both domestic and world production declined to lows of about 10,000 and 19,000 tons, respectively, in 1966. In 1964 and 1965 actual demands and predicted future demands for nuclear powerplants stimulated new exploration and mining, which resulted in increased production in 1967. This rejuvenation was short-lived, however, because predicted demands did not materialize, owing partly to delay of reactor deliveries and partly to public concern

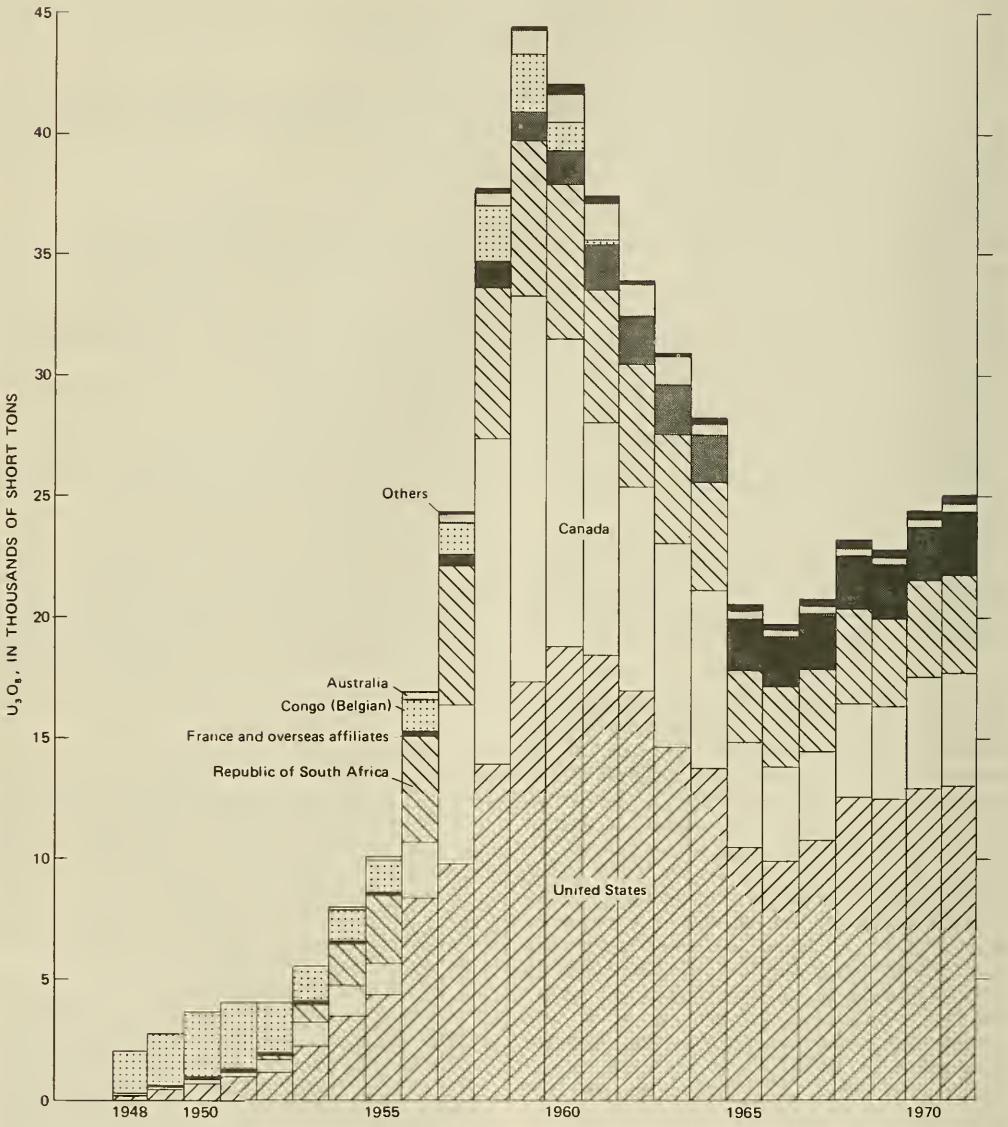

FIGURE 55.—Uranium production, 1948–71, from the United States, Canada, Republic of South Africa, France and African affiliates, Belgian Congo (now Zaïre), Australia, and other countries including Argentina and Sweden in most years, and Finland, West Germany, Portugal, and Spain in some years after 1956. Data from U.S. Atomic Energy Commission (1959), European Nuclear Energy Agency and International Atomic Energy Agency (1969, table 2), U.S. Bureau of Mines (1949–1972), and Williams (1971).

over safety and pollution hazards, and production leveled off in 1970 and 1971. Recently, concern over dwindling domestic oil and gas resources has increased new orders for nuclear reactors, and demand for uranium is expected to increase for many years.

Domestic production in the period 1948–71 totaled 229,913 short tons of U_3O_8, and reported world production, about 493,000 tons.

The chief source of domestic production was sandstone ores from the Colorado Plateau, Wyoming basins, and the Texas Coastal Plain; only about 5 percent came from vein and other deposits, mainly in Washington and Colorado. Small byproduct amounts came from copper leach solutions and from the processing of marine phosphorite to produce treble super phosphate (Bieniewski and others, 1971, p. 9). The phosphorite processing is significant because of the large resource in marine phosphorites. Outside the United States, sandstone ores are not an important source of uranium. Vein deposits are the chief uranium sources in Australia, the Congo, and France; Precambrian quartz-pebble conglomerates contain very large uranium reserves in South Africa and Canada.

Environmental problems in exploiting uranium deposits are those common to all milling, open-pit, and underground mining operations; an additional problem is the presence of radon gas in mines and tailings. Nuclear reactors produce plutonium, which is a hazardous material that requires very careful handling. They also produce radioactive wastes as well as large amounts of waste heat that require careful disposal. Nuclear plants, however, do not pollute the atmosphere as do oil- gas- and coal-fueled generators. The radioactive pollution hazards of nuclear reactors are not of the continuous type, but rather those of accidental spillage, seepage, fire, and explosion. With proper safeguards, nuclear powerplants affect the environment less than fossil-fueled types.

GEOLOGIC ENVIRONMENT

GEOCHEMICAL CYCLE

The uranium content of the crust of the earth is about 2 ppm (parts per million) and that of granitic rocks is about 4 ppm. Uranium originates in magmas where it is mostly in the tetravalent state. As magma crystallizes, the large size of the tetravalent uranium ion prevents it from entering the crystal lattices of common rock-forming minerals except as minor occlusions; instead part of it is deposited in an intergranular film on rock-forming minerals, enters accessory minerals, or forms its own minerals. The remaining uranium is concentrated in late magmatic differentiates, where some uranium forms its own minerals in pegmatites and veins. In veins, iron is commonly associated with uranium, and in some places copper, lead, zinc, molybdenum, and cobalt accompany uranium.

The accessory uranium-bearing minerals of igneous rocks generally resist oxidation, and weather out to be washed into detrital sediments, or under special circumstances, to become concentrated in placers, some of which contain appreciable uranium. On the other hand, the uranium-bearing films that form on minerals in igneous rocks and the uranium minerals in pegmatites and veins oxidize readily, and water-soluble hexavalent uranium is released to surface and ground waters. As these waters circulate through sediment some uranium may be absorbed by clay minerals and carbonaceous matter, and some is precipitated chemically or by evaporation. Reduction of hexavalent uranium to the tetravalent state and its subsequent precipitation from ground water is the mechanism by which the uranium deposits in sandstones are thought to have been formed. Iron is universally precipitated with uranium in this part of its geochemical cycle, and in some places copper, molybdenum, selenium, and chromium are similarly precipitated. Uranium-bearing waters also escape to the ocean where uranium may be precipitated with phosphatic sediments, taken up by organisms, or absorbed by carbonaceous mud. In the virtually oxygen-free atmosphere of early Precambrian time, it is postulated that uraninite from pegmatites and veins did not oxidize but rather formed placer concentrations, commonly with gold and thorium-bearing minerals.

MINERALOGY

Uranium in unoxidized black ores is tetravalent and in most such deposits it occurs in the minerals uraninite (UO_2) and coffinite [$U(SiO_4)_{1-x}(OH)_{4x}$] with pyrite as a common gangue mineral. The multiple oxides brannerite (oxide of uranium, titanium, thorium, rare earths, and other elements) and davidite (oxide of titanium, iron, and uranium) are the main uranium minerals in a few unoxidized ores. Tetravalent uranium substitutes for thorium and other elements in minerals such as monazite, uranothorite, multiple oxides of niobium, and tantalum, and for calcium in carbonate fluorapatite. It also occurs in unidentified organic compounds in many coaly rocks and marine black shales.

Under oxidizing conditions tetravalent uranium changes to hexavalent uranium and forms oxide,

vanadate, arsenate, silicate, sulfate, and carbonate compounds, most of which are hydrous and many of which are bright yellow or green. The vanadates, carnotite and tyuyamunite, are the most common and abundant.

TYPES OF DEPOSITS

Although anomalous uranium concentrations are widespread, concentrations of uranium that make minable deposits, ranging from about 400 to 2,500 times crustal abundance, are not common. Most identified resources are in a few kinds of rocks and geologic environments. The principal domestic recoverable resources occur as peneconcordant masses in continental and marginal marine sandstone and associated rocks. A small part is in coaly rocks and nonmarine limestone. Less than 2 percent of domestic resources occur in veins. Identified paramarginal and submarginal resources are chiefly in marine phosphorite and black shale and in igneous rocks. Some major foreign resources are in Precambrian quartz-pebble conglomerate.

PENECONCORDANT DEPOSITS

Peneconcordant deposits are widely distributed in the United States; they are especially numerous in some western States (Butler and others, 1962). Typically these deposits occur in sandstone lenses that are interbedded with mudstone. These strata accumulated under fluvial, lacustrine, and nearshore marine conditions in cratonic or marginal cratonic environments. Most of the host sandstone beds are quartzose and were derived from older sedimentary rocks; some, however, are arkosic and were derived mainly from granitic rocks. Volcanic ash is present in some of the host sandstone beds and is common in overlying and interbedded mudstone. Nearly all of the host sandstone beds contain carbonized plant matter or organic residues. The host beds range in age from late Paleozoic to Tertiary, but in any given area all or nearly all of the deposits are in one or a few favored stratigraphic units.

Uraninite and coffinite are the primary uranium ore minerals; carnotite and other secondary minerals are ore minerals in some deposits. The ore minerals mainly occupy the pore spaces of the sandstone, but in places they replace the sand grains or the carbonized plant fossils. The average grade of the ore mined ranged from about 0.15 to 0.30 percent U_3O_8; 0.08 percent U_3O_8 is a common grade cutoff for mining and little material below 0.08 percent is mined. Ore bodies range in size from small masses containing a few tons of ore to those containing more than 10 million tons. They occur in two distinct geometric forms: tabular bodies that are nearly concordant with the gross sedimentary structures of the host sandstone and roll bodies that are crescent-shaped and discordant to bedding in cross section and elongate in plan, with their long axes nearly concordant to bedding. The tabular deposits are discrete masses and tend to be clustered in favorable areas a few miles across; they are enclosed in reduced sandstone. The roll deposits are scattered along crescent-shaped interfaces between oxidized sandstone on the concave sides and reduced sandstone on the convex sides; in a given mining district an interface may extend for several miles and localize several ore bodies. Large deposits representative of the tabular type occur in the San Juan Basin, N. Mex. (Hilpert, 1969) and the Uravan mineral belt, Colorado (Motica, 1968); deposits representative of the roll type occur in the Shirley Basin, Wyo. (Harshman, 1968) and the Texas Coastal Plain (Eargle and others, 1971).

Many hypotheses have been proposed for the genesis of the deposits (Finch, 1967, table 8). Most geologists now think that the uranium was derived by leaching—either from volcanic glass within or overlying the host rock or from granitic terranes exposed along the margins of the sedimentary basins. Uranium was transported in ground water in the hexavalent state and precipitated under reducing conditions. Carbonaceous matter, H_2S gas, and transient sulfite derived from oxidation of preore pyrite are materials that have been cited as reductants that caused precipitation. Roll-type deposits apparently form at a dynamic interface between oxidizing and reducing conditions, that moves down the regional dip leaving altered (oxidized) host rock in its wake. In contrast, tabular deposits are wholly enclosed in reduced rock which in places may be completely surrounded by oxidized rock that is not in contact with ore.

DEPOSITS IN QUARTZ-PEBBLE CONGLOMERATES

Uranium-bearing Precambrian quartz-pebble conglomerates were deposited under deltaic or fluvial conditions in shallow basins in cratonic or marginal cratonic environments more than 2.3 billion years ago. It is postulated that in the nearly oxygen-free reducing atmosphere of early Precambrian time, rounded and polished detrital grains of uraninite and pyrite accumulated with the more typical detrital placer minerals. Although locally the placer forms of some uraninite and pyrite grains were later modified, both minerals are generally coextensive with conglomerate beds or coarse parts of conglomerates. The deposits are very large and extensive. In the

Blind River–Elliot Lake district, Canada, deposits containing uraninite and brannerite are 7–15 feet thick and from hundreds of feet to 2 miles across, and contain more than 5 million tons of ore. Minable grade averages 0.12–0.16 percent U_3O_8; gold values are 0.02–0.03 ounce per ton. The thorium-uranium ratio is 1:4 to 1:3 and some thorium has been recovered as a byproduct. In the Witwatersrand, South Africa, the deposits are larger and more extensive than at Blind River–Elliot Lake, but their uranium content is lower, generally 0.03–0.07 percent U_3O_8. Uranium is produced mainly as a byproduct of gold mining and locally as a coproduct. Ore minerals are uraninite with minor amounts of brannerite. Thorium is not recovered because of the small amount in the ore. Possibly similar deposits of undetermined magnitude have recently been identified in Precambrian rocks near Belo Horizonte, Brazil (L. A. Moura, Commissão Nacional de Energia Nuclear, Brazil, oral commun., 1972).

VEIN DEPOSITS

Uranium-bearing veins are fissure fillings in faults, joints, and fracture zones; they occur in many kinds of rocks ranging from Precambrian to Tertiary in age, and in diverse geologic settings. Ore occurs as tabular bodies, irregular stockworks, pipelike masses at fracture intersections, and in mineralized gouge and breccia. Chief types of alteration associated with uranium veins are sericitic, argillic, chloritic, and hematitic. Individual veins are a few inches to several feet wide and extend along strike and downdip as much as several hundred feet; these combine to form vein systems which extend as much as 1,300 feet below the surface in the United States and 5,000 feet in Canada and which contain 10 tons to millions of tons of ore. Average mined grade ranges from 0.10 to 1.0 percent U_3O_8. Deposits in which base-metal sulfides constitute appreciable to major amounts of the ore include the large deposits at Shinkolobwe, Zaïre (formerly Belgian Congo) and at Port Radium, Northwest Territories, Canada, both now depleted; and the moderate-sized deposits at Joachymov, Czechoslovakia, and at the Schwartzwalder mine, Colorado (Walker and others, 1963). Pyrite is the only abundant sulfide in the very large deposits at Beaverlodge Saskatchewan, Canada. Fluorite is a characteristic component of the moderate-sized deposits at Marysvale, Utah.

At Bancroft, Ontario, Canada, uraninite-thorite veins and irregular pods cut and replace bodies of unzoned granitic pegmatite and form fairly large deposits (Robinson and Hewitt, 1958). They contain an average of about 0.1 percent U_3O_8 and 0.025–0.2 percent ThO_2.

Veins are thought to have been deposited from hydrothermal solutions derived by differentiation of magmas. Uranium-bearing veins in the United States formed mainly during Late Cretaceous to late Tertiary time.

OTHER EPIGENETIC DEPOSITS

A few major epigenetic deposits do not fit into the preceding groups. The Midnite mine, Washington, is in Precambrian metasedimentary rocks along their contacts with Cretaceous granite. Individual ore bodies are as much as 200 feet wide, 700 feet long, and more than 150 feet thick. The average mined grade is about 0.23 percent U_3O_8. The deposit probably was formed shortly after granitic intrusion, by hydrothermal solutions directed along favorable zones adjacent to the intrusive contact (Becraft and Weis, 1963). At the Ross Adams mine in southeastern Alaska, numerous uraninite- and thorium-bearing veinlets cut peralkaline granite in which abundant uranothorite and uranoan thorianite occur as late crystallizing accessory minerals (MacKevett, 1963). This deposit has yielded about 70,000 tons of ore that averaged more than 0.60 percent U_3O_8. Although the uranium-thorium ratio is about 1:1, thorium has not been recovered.

Deposits in this miscellaneous group in foreign areas include: (1) A several-million-ton irregular pipelike body of uraninite and uranophane disseminated in brecciated syenitic rock at the Gunnar mine, Beaverlodge area, Saskatchewan, Canada, (2) a subhorizontal, irregular, tabular body of mineralized metamorphic rock at Rabbit Lake, Saskatchewan (H. W. Little, Geol. Survey of Canada, oral commun., 1972), and (3) probably the Nabarlek, Jim Jim, and Ranger deposits in older Precambrian rocks discovered recently in the Northern Territory, Australia.

URANIFEROUS IGNEOUS ROCKS

In the United States, only small amounts of uranium have been mined from pegmatites, most of which are the zoned type.

Aside from pegmatites, a few igneous rock bodies contain anomalous concentrations of uranium as an indigenous constituent. The biotite phase of the Conway Granite of Triassic or Jurassic age in central New Hampshire contains an average of 0.0015 percent U_3O_8 over a 300-square-mile area. It also contains about 0.0064 percent ThO_2. (See under Thorium in this chapter.)

Bodies of a variety of uraniferous igneous rocks in other countries are mostly smaller but richer in uranium than the Conway granite. They include

pyrochlore-bearing alkalic rocks at Araxa, Brazil, and in Ontario, Canada (Rowe, 1958); sodalite foyaite and nepheline syenite near Julianehaab, Greenland (Bondam and Sörensen, 1958); riebeckite granite in Nigeria; and alaskitic rock near Rössing, South West Africa.

URANIFEROUS PHOSPHATIC ROCKS

Most phosphatic rocks are uraniferous and their uranium content generally increases with the phosphate content. Marine phosphorite is the dominant source of phosphate and constitutes a very large resource of uranium. In such rocks, geosynclinal facies tend to be more uraniferous than platform facies. Uraniferous marine phosphorite deposits, commonly 5–10 feet thick, underlie hundreds of square miles, and their uranium content generally ranges from 0.007 to 0.07 percent U_3O_8. Phosphorite beds in the Phosphoria Formation of Permian age underlie 135,000 square miles of Idaho, Montana, Utah, and Wyoming (McKelvey and Carswell, 1956). Their uranium content ranges from 0.001 to 0.075 percent U_3O_8, but beds more than 3 feet thick and with more than 31 percent P_2O_5 generally average 0.012–0.024 percent U_3O_8. Prosphorite in the Bone Valley Formation of Pliocene age in the land-pebble phosphate field in Florida ranges in thickness from 6 to 7 feet over several hundred square miles and averages 0.012–0.024 percent U_3O_8 and 20–30 percent P_2O_5 (Altschuler and others, 1956). Uranium in marine phosphorite deposits was probably deposited from sea water during sedimentation, or in some places possibly later by downward percolating ground water.

Large portions of extensive deposits of marine phosphorite in countries along the Mediterranean Sea from Morocco to Israel contain at least 0.01 percent U_3O_8 (Davidson and Atkin, 1953). Near Recife, Brazil, deposits of phosphorite somewhat like those in Florida yield phosphate products that contain 0.02 percent U_3O_8. Phosphorite that fills large depressions formed by solution of dolomite in Central African Republic are also uncommonly rich in uranium (Mabile, 1968). Deposits of aluminum phosphate in Senegal and Nigeria are also uraniferous. Marine phosphorite of Cambrian age in the Kara-Tau Mountains, Kazakhstan, U.S.S.R., resemble the Phosphoria Formation and are probably uraniferous.

URANIFEROUS MARINE BLACK SHALES

Many marine black shales rich in organic matter contain minor amounts of uranium that was deposited under anaerobic conditions with the organic fraction of the shale during sedimentation in shallow epicontinental seas. Most of the identified domestic black shale resources are in the upper member of the Chattanooga Shale of Late Devonian and Early Mississippian age in central Tennessee and adjacent Kentucky and Alabama (Swanson, 1961). This member is 12–18 feet thick over an area of about 4,000 square miles, and averages about 0.007 percent U_3O_8. Moreover, the Chattanooga and its correlatives underlie about 800,000 square miles extending from eastern Tennessee to Texas and Montana; its uranium-bearing strata average about 40 feet in thickness and about 0.0035 percent U_3O_8 in grade. In Sweden, black shale of Late Cambrian and Ordovician age, which is 9–18 feet thick, is unusually rich in uranium and averages about 0.03 percent U_3O_8 (Svenke, 1956). Radioactive shale of the same age in the U.S.S.R. near the Baltic Sea may not be as rich as that in Sweden, but no modern determinations of its uranium content have been announced.

RESOURCES

IDENTIFIED AND HYPOTHETICAL RESOURCES

Both identified and hypothetical uranium resources can be divided into three subclasses: (1) recoverable resources, those that can be extracted profitably under 1972 economic conditions, (2) paramarginal resources, here defined as those that might be extracted profitably with a 50-percent to 5-fold increase in the price of U_3O_8, and (3) submarginal resources, those that require more than a 5-fold price increase. Nearly all of the domestic recoverable resources can be produced as a sole or principal product of mining operations, but they represent only a small fraction of the total identified resources. Most of the much larger paramarginal and submarginal resources are not likely to become major sources of uranium in the near future—either because the technology of extraction is costly or unsolved, because limits on land use might restrict mining large volumes of material, or because the most nearly economically recoverable uranium can be obtained only as a byproduct.

RECOVERABLE RESOURCES

The identified recoverable resources in the United States totaled 273,000 tons of U_3O_8, as of December 31, 1971 (table 93) and are in rock averaging about 0.22 percent U_3O_8 (4 lb. U_3O_8 per ton). Of this total, more than 99 percent—270,800 tons—is in peneconcordant deposits in sandstone and related rocks, and the remaining 2,200 tons is in veins and other types of deposits. About 50 percent of these resources is in northwestern New Mexico, about 35 percent in Wyoming, about 5 percent in Texas, about 3 percent

TABLE 93.—*Identified uranium resources in the United States and other countries that have reported resources*

[Identified resources are specific, identified mineral deposits that may or may not be evaluated as to extent and grade, and whose contained minerals may or may not be profitably recoverable with existing technology and economic conditions]

Locality	Type of deposit	Grade (percent U_3O_8)	Short tons U_3O_8	Source of data
United States: western States	Peneconcordant in sandstone, vein.	0.22	273,000	U.S. Atomic Energy Comm. (1972b).
Canada:				
Blind River-Elliot Lake, Wollaston Lake, Bancroft, Beaverlodge.	Precambrian conglomerate, veins, and other types.	>.10	230,000	Sherman (1972).
Elliot Lake	Precambrian conglomerate.	<.10	130,000	Sherman (1972).
Mexico: Chihuahua (Aldama) and other States	Peneconcordant in sandstone, vein.	>.10	2,380	Sherman (1970).
Argentina: Salta, Mendoza	Sandstone.	>.10	9,000	European Nuclear Energy Agency and International Atomic Energy Agency (1969).
France: Vendée, Limousin, Forez, Morvan	---do	>.10	66,400	Sherman (1972).
Portugal: Viseu (Urgeirica), Nisa, Guarda	---do	>.10	9,500	European Nuclear Energy Agency and International Atomic Energy Agency (1969).
Spain: Ciudad Rodrigo (Salamanca), Andujar	---do	>.10	11,000	European Nuclear Energy Agency and International Atomic Energy Agency (1969).
Sweden: Västergötland (Billingen), Närke	Marine black shale.	.03	350,000	Sherman (1972).
Other Europe: West Germany, Italy, Turkey, Yugoslavia	Vein, peneconcordant in sandstone.	>.10	6,500	European Nuclear Energy Agency and International Atomic Energy Agency (1969).
Central Africa Republic: Bakouma	Phosphatic-filling karst in Precambrian dolomite.	~.10	19,500	Sherman (1972).
Gabon: Mounana (Franceville), Mikouloungou	Structural controlled dissemination in Precambrian sandstone.	>.10	19,500	Sherman (1972).
Niger: Arlit	Peneconcordant in sandstone.	.29	26,000	Sherman (1972).
Azelick, Madaouela	---do	>.10	13,100	Sherman (1969).
South Africa, South West Africa: Witwatersrand, Rössing	Precambrian conglomerate, igneous rock.	<.10	300,000	Sherman (1972).
Australia: Mary Kathleen, Alligator Rivers area (Nabarlek, Jim Jim, Ranger), Frome Lake.	Vein and other types.	>.10	100,000	Sherman (1971).
India: Jaduguda, Bihar	Vein.	.06–.07	36,000	Mining Journal (1971).
Japan: Ningyo-Toge	Peneconcordant(?) in Miocene and Pliocene conconglomerate.	.06	4,000	European Nuclear Energy Agency (1965).
Total		------	1,605,880	

each in Colorado and Utah, and the rest in a few other Western States.

These identified recoverable resources, plus several thousand tons of U_3O_8 that might be recovered each year as a minor byproduct from phosphate rock and some copper ores, are adequate to satisfy estimated domestic requirements to the early 1980's, and most of these resources will be mined by that time.

Recoverable uranium resources outside the United States listed in table 93 are largely in Precambrian conglomerate and in vein and related types. Most of these deposits average more than 0.10 percent U_3O_8 and may be mined for their uranium content alone. Sweden recovers uranium from black shale deposits having an uncommonly high grade for black shale of 0.03 percent U_3O_8 (table 93). In the Witwatersrand, South Africa, uranium is a byproduct or coproduct

of gold mining. Part of the African resources are probably paramarginal because of their remote location.

The total identified recoverable uranium resources of countries listed in table 93 is about 1.6 million tons of U_3O_8, which is enough to supply the estimated world demand until the late 1980's.

Uranium resources in the U.S.S.R., China, and some other Asiatic and eastern European nations not listed in table 93 occur in deposits similar to those found in North America. Data on identified resources for these areas are not available. It is known, however, that in the U.S.S.R., peneconcordant uranium deposits occur in unspecified localities, and uranium-bearing veins occur in the Ukrainian region and elsewhere.

Domestic hypothetical recoverable resources are estimated to total about twice the identified recoverable resources, or about 500,000 tons. If these resources are found by continued exploration and are mined, as expected, they will satisfy the estimated domestic requirements only until the early 1990's. After that, the domestic requirements, which will gradually decrease if the fast-breeder reactors are developed or will continue to increase if they are not, will have to be satisfied by importing much of the uranium needed or by mining much lower grade uranium resources at a high unit cost.

CONDITIONAL RESOURCES

Peneconcordant sandstone deposits and vein deposits contain about 200,000 tons of U_3O_8 classified as identified paramarginal resources. These resources, which are too lean to be mined at present prices, are mostly adjacent to minable ore bodies where they would be bypassed in mining, and subordinately in separate deposits. The material adjacent to minable ore bodies would be very costly to recover by conventional mining methods after mine openings are abandoned and caved; perhaps, however, techniques of solution mining can be developed to recover some of this uranium at moderate cost. Alternately, a scheme to subsidize the extraction and stockpiling of the low-grade material that is being bypassed in current mining operations might be justifiable to conserve a resource that will be much needed in the future.

Other conditional resources consist of small amounts of uranium concentrated in certain types of rocks that are moderately abundant, and although the amount of uranium in a single ton of these rocks is small, the total amount of uranium contained in them is indeed large. The uranium in such rocks should be considered in appraising uranium resources, provided some of the factors limiting its availability are appreciated. These factors are chiefly price, technology, and byproduct status.

Where the amount of uranium per ton of rock is small, the recovered U_3O_8 is necessarily expensive. Such high-cost uranium must compete with possible substitutes, including less expensive uranium from domestic or foreign sources, thorium, and fossil fuels. The abundance of coal, gas, and oil as alternate fuels for the generation of electricity in the short term and the possible increase in use of thorium in nuclear reactors (see "Thorium") will effectively limit the price that will be paid for uranium. Consequently many domestic low-grade uranium deposits will not be a source of uranium in abundance for many decades to come.

Whether much of the uranium in low-grade deposits becomes an available resource depends heavily on developments in metallurgical and other technology. For some types of deposits the technology of recovery has not yet been developed; from others the uranium can be recovered but only at considerable expense. The development of new recovery methods and the improvement in the efficiency of others will determine how soon and how much of the low-grade deposits become an available resource.

The supply of uranium recovered as a byproduct in the production of another commodity is determined by the amount of the prime commodity produced. It can be increased only as the markets for the prime commodity expand.

Factors such as the foregoing, which limit availability of conditional resources, must be borne in mind in connection with the ensuing discussion of the large low-grade uranium resources in the United States.

Marine phosphorites in the United States contain large uranium resources. The Phosphoria Formation in Idaho and adjacent States is estimated to contain identified paramarginal resources of about 700,000 short tons of U_3O_8 in rock with an average grade of not less than 0.012 percent U_3O_8 (0.24 lb U_3O_8 per ton) and not less than 31 percent P_2O_5 (V. E. McKelvey, written commun., 1951). Identified paramarginal resources in the Bone Valley Formation in Florida are estimated to be about 300,000 short tons of U_3O_8 in phosphate rock products of about the same grade as in the Phosphoria (Altschuler and others, 1956; J. B. Cathcart, written commun., 1951). Additional marine phosphorites in Idaho and North Carolina are estimated to contain identified submarginal resources of about 5 million short tons of U_3O_8 in rock whose grade ranges from about 0.006 to about 0.012 percent U_3O_8 (0.12–0.24

lb U_3O_8 per ton) (V. E. McKelvey, written commun., 1951; J. B. Cathcart, written commun., 1965). Domestic hypothetical paramarginal uranium resources in marine phosphorite are estimated at about 250,000 short tons of U_3O_8, and submarginal, about 1 million short tons, both mostly in western States. A very small amount of the total resources in phosphorite can be obtained at moderate cost as a byproduct of making fertilizer, but to obtain more uranium would require mining and treating this rock principally for uranium; unit costs would be high and vast quantities of rock would have to be moved to obtain a significant amount of uranium.

Phosphorite deposits are being mined for phosphate but their contained uranium is not being recovered. Uranium in rock that is used to make elemental phosphorus by the electric furnace method goes mostly into the silicate slag. A process for recovering uranium from the slag has not been developed. Most of the uranium in phosphorite that is used to make fertilizer by the wet-process phosphoric acid method stays in the fertilizer and is lost as a resource when the fertilizer is used. Marine phosphorite from Florida was the source of about 500 tons of U_3O_8 recovered between 1953 and 1961 as a minor byproduct from phosphoric acid made by the wet-process method. Recovery was discontinued because of costs uncompetitive with uranium from sandstone ores. Bieniewski, Persse, and Brauch (1971) estimated that, if Florida phosphate rock containing 0.012 percent U_3O_8 were treated by the wet-process method at the expected rate of fertilizer production, about 85,000 tons of U_3O_8 could be recovered between 1971 and 2000 at a cost of slightly more than $10 per pound.

Residues of copper smelting are also a potential source of byproduct uranium at about the same cost as that from phosphate rock. Bieniewski, Persse, and Brauch (1971) estimated that about 30,000 tons of U_3O_8 could be recovered during the next 30 years by leaching residues containing 0.0001–0.0012 percent U_3O_8. Although byproduct uranium recovered in manufacturing fertilizer and from smelter residues would help to meet requirements, the amount that could be obtained most economically is limited by the production rate of the principal commodities.

Marine black shales are a common rock, and they generally contain low concentrations of uranium. Of all the black shale beds of minable thickness that have been sampled in the United States, the Chattanooga Shale in eastern Tennessee contains the highest concentration of uranium, but only 0.007 percent U_3O_8 (0.14 lb U_3O_8 per ton). It represents a submarginal resource of about 7 million tons of U_3O_8, but to obtain any significant part of this resource would require mining vast areas by open-cut and underground methods; unit costs would obviously be high. More than twice as much uranium is present in this formation in other parts of Tennessee and adjacent States, but at concentrations only about half that in eastern Tennessee. Even more uranium is present in the Chattanooga and its correlatives in the midcontinent where they are deeply buried, but the uranium content of these rocks is leaner, and less well defined, than it is in the more restricted areas.

Most igneous rocks contain a little uranium, representing the order of crustal abundance—0.0002–0.0004 percent U_3O_8—but some bodies of igneous rock are appreciably richer and thus might qualify as a potential resource. Of the igneous bodies that have been sampled in the United States, those of syenite and associated pegmatite in the Bearpaw Mountains, Mont., and the Conway Granite in New Hampshire are favorable examples. Those rocks in the Bearpaw Mountains are in relatively small bodies, but they average 0.05 percent U_3O_8 (1 lb per ton), and are estimated to contain a paramarginal resource of about 12,500 tons U_3O_8. The Conway Granite is exposed over an area of about 300 square miles and contains 0.001–0.003 percent U_3O_8 (0.02–0.06 lb per ton). This body of granite to a depth of 1,000 feet (representing almost 50 cubic miles of rock) is estimated to contain about 7½ million short tons of U_3O_8. Hypothetical uranium resources in igneous rocks have not been estimated.

If bodies of rock like the phosphate deposits, black shales, or igneous rocks are ever seriously considered as possible sources of domestic uranium, it might be possible to develop recovery processes to extract other useful commodities along with uranium, which might reduce to some extent the unit cost of the uranium recovered. Nevertheless, if significant quantities of uranium are sought from these sources, vast quantities of rock would have to be mined and treated, which would require much energy and would temporarily disrupt large areas of ground.

No attempt is made here to evaluate worldwide conditional uranium resources in phosphorites and black shales; they are known to be very large.

Hypothetical resource figures are not available for most nations outside the United States. However, in view of the wide occurrence of deposits akin to those in North America, it is postulated that in areas of continental size the uranium resources bear the same relation to the size of the area as the uranium resources of North America bear to its area.

Sea water contains 0.00015–0.0016 ppm uranium.

Although that is a low concentration, the total amount of uranium in sea water is very large (European Nuclear Energy Agency, 1965). It seems reasonable to suppose that a small amount of byproduct uranium will be recovered in the near future from desalination plants or from plants recovering magnesium from sea water.

SPECULATIVE RESOURCES

Domestic speculative resources consist of (1) new districts containing types of uranium deposits found elsewhere in the United States, (2) types of deposits known only elsewhere in the world, and (3) new types of deposits.

The margins and locally the axial parts of sedimentary basins, particularly those containing sediments derived from either granitic terranes or volcanic ash, are favorable targets in the search for new uranium districts. These basins may be either intermontane such as in Wyoming, or of the gulf type as exemplified by the coastal plain in Texas where shoreline-facies rocks contain major deposits. Although both of these basins are Tertiary in age, analogs in older rocks, especially Cretaceous, ought to be equally favorable.

Unconformities related to paleokarst topography may be favorable sites for occurrence of large uranium deposits. Two types of deposits are known in this setting. A large deposit of Cretaceous uranium-bearing phosphatic rock reportedly fills paleokarst developed in Precambrian dolomite in Bakouma, Central African Republic, and small deposits of tyuyamunite-bearing breccia occur in cavities related to karst developed on the Madison Limestone in the Pryor Mountains, Mont. Exploration here and elsewhere in this environment may be fruitful.

Ancient, 2.0–2.4 b.y. (billion years) old, Precambrian quartz-pebble conglomerates analogous to those that contain the Witwatersrand and Blind River–Elliot Lake uranium deposits do not crop out in the United States. This type of rock might be present, however, somewhere in the deep subsurface of North and South Dakota and the east half of Montana, where, according to Goldich, Lidiak, Hedge, and Walthall (1966), the ancient continental crust was formed more than 2.5 b.y. ago.

Theoretical considerations and the description of the Rössing deposit in South West Africa suggest that there may be "porphyry" uranium deposits similar to porphyry copper and molybdenum deposits. Porphyry uranium deposits would be late magmatic differentiates—for example, alaskites and associated pegmatites—and would be easiest to recognize in arid or semiarid regions.

PROSPECTING TECHNIQUES

Radiation counters are the commonest tools used in prospecting for uranium. They are of two main types: (1) Geiger counters, which are normally portable and are designed to count γ radiation alone, and β plus γ radiation, and (2) scintillometers, which count only γ radiation and which may be portable, carborne, or airborne. Scintillometers are more sensitive and respond faster than Geiger counters. If uranium only is present and is in equilibrium with all the daughter products of its radioactive decay, both types of instruments may be calibrated to indicate uranium content. However, if the uranium is not in equilibrium, they may indicate either more or less uranium than is present. In places where uranium has been leached but its daughter products remain, it is possible to detect radiation where there is little or no uranium. Conversely, recently deposited uranium that is too young (less than 500,000 years old) to be in radioactive equilibrium, emits so little β and γ radiation that a deposit may contain more uranium than is indicated by its β and γ count. Standard Geiger counters and scintillometers cannot distinguish uranium from thorium, or from naturally occurring radioactive potassium-40.

Radiation counters are also used in drill-hole exploration. Only γ radiation can be detected in drill holes because β particles lack the energy to pass through the water which is usually in the hole or through the walls of the detecting instrument. Scintillometers are used to probe drill holes because of their greater sensitivity and faster response. Resistivity and spontaneous potential surveys of drill holes are also customarily run. These two geophysical methods do not indicate uranium directly, but can be interpreted to distinguish sandstone from shale and to indicate relative porosity. The identification of shale at the site of a small γ anomaly strongly suggests that the anomaly is caused by potassium-40 in the shale.

Airborne radiometric surveys using the total count method have proved useful in prospecting for uranium. In this method the scintillometer records total γ radiation and does not discriminate between uranium, thorium, and potassium-40 sources. Total count anomalies have to be ground checked to determine if uranium causes the anomaly. Airborne gamma-ray spectrometry, which has been developed in recent years, distinguishes between uranium, thorium, and potassium-40 by measuring γ radiations at particular energy levels. Thus, the strong γ-emitting daughters of U^{238} and Th^{232}, Bi^{214} and Tl^{208}, respectively, are used to distinguish uranium and thorium;

the γ spectrum of potassium-40 is used for potassium-40.

Other direct methods that have been used in prospecting for uranium are water analyses and geochemical sampling of soil and colluvium. Anomalously large amounts of uranium in water have led to the discovery of a few deposits, but in most places water analyses have not been a successful prospecting tool. Many natural waters contain anomalous amounts of uranium even though no uranium deposits are known in the vicinity.

Under development is an indirect technique that uses the Eh and pH of water to evaluate sandstone aquifers and to locate favorable areas for exploration. If oxidation-reduction interfaces are important factors in the formation of uranium deposits in sandstone, then with further development and refinements this technique may be a useful exploration tool.

Radon, an alpha-emitting gas and one of the daughter products of uranium, has been used as an indirect aid in prospecting for uranium. Scintillometers and alpha-sensitive film have been used to detect its presence.

The indirect method of magnetic prospecting has been used without much success in looking for uranium deposits in continental sandstones. If the uranium were concentrated in stream channels and were associated with heavy detrital minerals, particularly magnetite, then the magnetic method might be a useful tool.

PROBLEMS FOR RESEARCH

The sedimentary framework of basins containing major uranium deposits in sandstone formations should be studied in order to develop new guides for finding new districts in these and other basins. Particular effort should be made to determine: (1) The original boundaries and configuration of basins, especially any intraformational basins within thick sequences of rocks, (2) the location, relief, and rock types of bordering uplands, (3) the diagnostic characteristics of the proximal, midfan, and distal rock facies between the margins and center of basins, (4) the ancient and modern hydrologic conditions, and (5) the postsedimentary histories.

The differences and similarities between tabular deposits, such as found in the Colorado Plateau region, and roll-type deposits, found in Wyoming Tertiary basins, should be studied. Comparative studies of alteration patterns and the sedimentary framework of each type are needed. Colorado Plateau deposits should be examined for possible evidence of vestiges of roll-type bodies that may have been developed at an early stage in the formation of the ore bodies. If evidence of early ore bodies is found, then redistribution of uranium during compaction, consolidation, and lithification of the host rock should be investigated. Results of the study could guide exploration for and aid resource evaluation of undiscovered districts in the Plateau region, and especially in Mesozoic and Paleozoic rocks elsewhere.

The geology of uranium-bearing veins in the United States should be studied in the hope of increasing our relatively small resources of this type. Knowledge of the geology and distribution of the large vein deposits in Canada may aid this research.

Continued research is needed on the development of cheaper methods of extraction of uranium from paramarginal and submarginal resources in marine phosphorite and black shale and igneous rocks.

The applicability of geochemical and other methods for prospecting and exploring for uranium should be improved by additional research.

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THORIUM

By Mortimer H. Staatz and Jerry C. Olson

ABSTRACT OF CONCLUSIONS

Although the current demand for thorium is small, future needs may be large as a fuel for nuclear generators. The occurrence of thorium is widespread, and large deposits are found in beach and fluviatile placers, veins, sedimentary rocks, alkalic igneous rocks, and carbonatites. Thorium has been produced principally from monazite from beach and fluviatile placers, although in the 1950's and early 1960's monazite from a unique vein in South Africa was the chief source. In the early 1970's monazite was recovered principally as a byproduct of titanium or tin mining in India, Brazil, Australia, and Malaysia. A large thorium resource in the conglomerates at the Elliot Lake uranium mines, Canada, could become an important byproduct if demand increases. Thorium resources are not well known because of the small demand, but are sufficient for many years in the future. The development of a viable domestic thorium mining industry is dependent on a large enough increase in demand to exceed the amount obtainable as byproducts from other types of deposits.

INTRODUCTION

Thorium is a heavy, ductile, silver-gray metal that, like uranium, is the parent of a series of radioactive decay products, ending in a stable isotope of lead.

Current demand for thorium is small, and in 1968 was only about 125 tons of ThO_2 (Stevens, 1969, p. 1068). Of this amount, 50 percent was used in making gas mantles, 30 percent in magnesium alloys, 10 percent in dispersion-hardened metals, and the rest in specialized refractories, polishing compounds, electronic devices, and chemicals. The demand for industrial uses, although small, will continue inasmuch as satisfactory alternate materials are not

known for most of thorium's uses, especially in gas mantles and in alloys (Shortt, 1970, p. 209). Being radioactive, thorium has considerable potential as a nuclear fuel. It cannot, however, be used directly in a nuclear reaction, because it does not contain fissionable isotopes to start the reaction; bombardment by neutrons from fissionable U^{235} converts thorium to fissionable U^{233}. Five types of thorium-cycle reactor systems have been investigated by the U.S. Atomic Energy Commission (Stevens, 1969, p. 1072). The farthest advanced of these is the HTGR (high-temperature gas-cooled reactor). A 40-MWE (megawatts electrical) prototype of the HTGR was put into operation by Philadelphia Electric at Peachbottom, Pa., in 1966. The first reactor designed specially for commercial use is near Platteville, Colo., where Public Service Co. of Colorado has a 330 MWE HTGR that is expected to start producing electricity in April 1973. Four other HTGR reactors have been ordered—two of 770 MWE by Delmarva Power and Light Co. and two of 1,100 MWE by Philadelphia Electric. The HTGR has a number of technical advantages over the uranium reactors now in use—it is more efficient to operate, runs on cheaper fuel, and produces less thermal pollution. The Public Service Co. of Colorado's HTGR will have an efficiency of 39 percent, which is on a par with the best coal-operated electric generators and is better than the best uranium generators in use in 1971, which have 34 percent efficiency.

EXPLOITATION

Thorium was discovered by Berzelius in 1828, but the first real demand for the element was created after Carl Auer von Welsbach invented the thoriated incandescent gas mantle in 1891. The only common thorium mineral known at that time was monazite. Although monazite is also a principal source of rare earths, monazite production from 1895 to 1921 (fig. 56) reflects the demand for ThO_2 and minor amounts of CeO_2 used in the gas mantle industry (Olson and Overstreet, 1964, p. 3). Monazite production in the United States prior to 1909 came principally from stream placers in North and South Carolina, and about equalled the country's demand. The rest of the world production came chiefly from beach placers in Brazil. From 1912 to 1945 the large beach placers in India produced a major part of the world's monazite. After 1920 the use of ThO_2 in gas mantles declined (fig. 56), and the little monazite produced between 1921 and 1934 was used largely for its rare earth content. Before World War II, uses and production of both rare earths and thorium increased. Because thorium is a radioactive material, India and Brazil nationalized their monazite deposits in 1946 and 1951, respectively, and restricted monazite exports during the period in which the United States was building up its stockpiles. The difference in demand was taken up by monazite from beach placers, chiefly in Australia, Malaysia, South Korea, Indonesia, United States, and Malagasy, and from a unique vein deposit in South Africa. Both India and Brazil resumed monazite mining, but separated the thorium and rare earths from the monazite in local plants. The thorium was not exported, but foreign markets were sought for the rare earths (Overstreet, 1967, p. 10). During the 1950's and 1960's monazite was mainly a byproduct of titanium (ilmenite or rutile) mining in Australia, India, and United States and of tin in Malaysia and Indonesia. The only nonplacer monazite mined came from a vein 13 feet thick exposed for 900 feet on the Steenkampskraal farm in Cape Province, South Africa (Pike, 1958, p. 92). This vein consists of 80 percent monazite and apatite, and veins of this type have not been reported elsewhere. About 51,100 tons of monazite were shipped from this property between 1952 and 1959 to Lindsay Chemical Co. in the United States and 8,000 tons in 1962 and 1963 to American Potash and Chemical Corp. Because of production from this mine, South Africa largely dominated the monazite market during these periods (fig. 56), but at present it is shut down.

Data on the amount of ThO_2 actually obtained from monazite production during various years are not always obtainable, for two principal reasons. One is that the amount of ThO_2 ranges from 0 to 31.5 percent in various monazites (Overstreet, 1967, p. 1), or from about 3.5 to 9.0 percent in commercial monazite concentrates (Parker and Baroch, 1971, p. 67). The ThO_2 content of monazite from each geographical area, however, commonly falls within relatively short ranges. The other principal reason is that in some years, such as the late 1960's, monazite is sold principally for its rare earth content, and the amount of ThO_2 actually produced is not known.

Monazite was practically the only source of thorium prior to 1953. Since that time thorium has also been recovered as a byproduct from the following two types of uranium ores:

1. In Malagasy, from 1953 to 1968, relatively small, rich uranothorianite deposits yielded 4,170 short tons of concentrates that averaged about 60 percent ThO_2 (Parker and Baroch, 1971, p. 68). These concentrates were produced principally by the French Atomic Energy Commission and shipped to France. This amount of ThO_2 is about twice the amount used in the

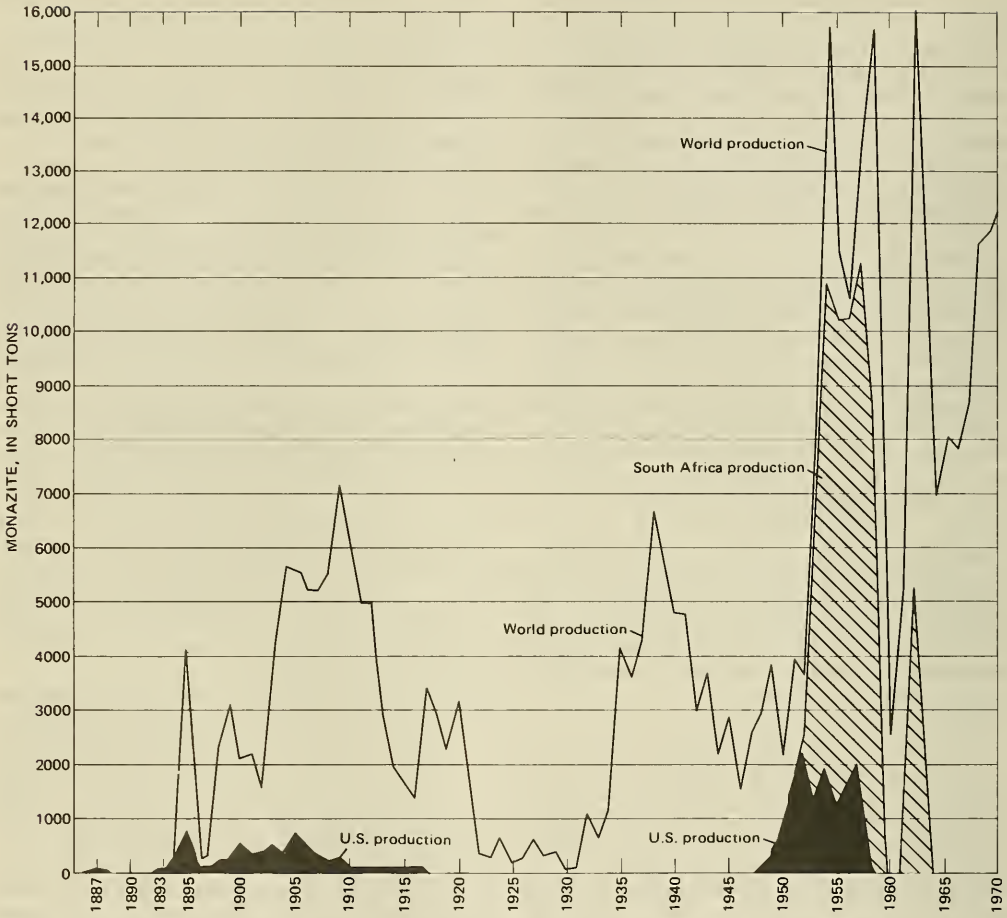

FIGURE 56.—United States, South African, and world production of monazite, 1887–1970. Data for 1887–1947 from Olson and Overstreet (1964, fig. 1); 1948–70, from U.S. Bureau of Mines (1950–72).

United States from 1947 through 1968 for nonenergy uses.

2. Near Elliot Lake, Canada, thorium was first recovered from Precambrian uranium-bearing conglomerates in 1959, from ore containing about 0.05 percent ThO_2 (Williams, 1969, p. 487). The thorium was recovered from effluent solutions by ion exchange following the removal of the uranium, and was precipitated as a concentrate that contained 25–40 percent ThO_2. The ThO_2 was recovered from only a small part of the uranium ore mined. Thorium shipments in Canada in the period 1966–69 contained a total of about 186 tons of ThO_2, only a small part of the capacities of the mills, but lack of market caused production to cease in 1968. Most of the concentrates were shipped to Thorium Ltd. in Great Britain, although some was shipped to the United States and some was used in Canada for making thorium metal.

In 1957, 132 tons of thorium-bearing ores was re-

covered principally from pegmatites; and in 1958, 650 tons of thorite concentrate was obtained from thorite-bearing quartz-carbonate veins in Colorado (Kelly, 1962, p. 3).

The principal placers that have been mined for monazite in the southeastern United States are small fluvial placers in the Piedmont of North and South Carolina. The value of the land for agricultural purposes is commonly greater than for monazite placer mining. The changes in land use and the small size of many of the deposits deter the operation of most fluvial placers. In some of the larger beach placers from South Carolina to northern Florida, the value of residential property would deter their use as beach placers. For example, Hilton Head Island, S. C., where 8,266,000 tons of heavy minerals containing approximately 2,880,000 tons of ilmenite and 94,600 tons of monazite were reported (McCauley, 1960, p. 5–6), is covered by many fine estates, golf course, and summer residences.

GEOLOGIC ENVIRONMENT

GEOCHEMISTRY

Recent estimates of the thorium content of the earth's crust range from about 6 to 13 ppm. Most of the thorium is widely disseminated in small quantities which vary in amount in different rocks. In its geochemical cycle, thorium becomes concentrated during several episodes, for example:

1. In magmatic intrusion and differentiation, because of its relatively large ionic radius and high valence thorium tends to become concentrated in the residual solutions as crystallization progresses. Thus it is most abundant in the younger members of rock series such as granitic and alkalic rocks and other rocks formed from residual magmatic fluids. The thorium content of granitic rocks that approach true granite in composition is likely to be higher than that of granodiorite or quartz monzonite, and it is notably high in some small alkalic rock complexes with which carbonatite and fenite are associated. During magmatic and metamorphic processes, therefore, thorium may be concentrated in veins, carbonatite, pegmatite, and certain alkalic rocks, granites, and metamorphic rocks.
2. In magmatic and metamorphic phases, the type and grade of metamorphism are factors in determining whether monazite, the principal ore mineral of thorium, is formed, and in determining the thorium content of the monazite. Thus the higher grade metamorphic and related igneous terranes are the best source areas for monazite with a high thorium content.
3. During weathering and erosion, monazite tends to remain as detrital grains owing to its insolubility and high specific gravity. The weathered mantle thus becomes enriched in this and other residual heavy minerals, which gradually move downslope and downstream, forming local placer concentrations. Monazite and other heavy minerals that reach the sea are deposited chiefly near shore at the mouths of rivers, but some thorium is also adsorbed on clay minerals during weathering and becomes disseminated in clayey sediments. During weathering and erosion, therefore, thorium may be concentrated in residual, stream (valley) placer, or beach placer deposits. Detrital mineral deposits formed in these ways may also be preserved in ancient sedimentary rocks under proper conditions, or on erosion of them the monazite may be reconcentrated to form rich, second-generation placer deposits.

ORE MINERALS AND ASSOCIATED MINERALS

The chief ore minerals of thorium are monazite [$(Ce,La,Nd,Th)PO_4$], thorite, ($ThSiO_4$), uranothorite, and brannerite (a multiple oxide of Ti, U, Ca, Fe, Th, and Y). Other thorium-bearing minerals present in some deposits include allanite; multiple oxides such as euxenite, samarskite, fergusonite, and betafite; and thorianite (ThO_2). Thorium is commonly associated, in minerals and in deposits, with the rare earths, niobium, titanium, and zirconium; thorium may occur with these elements as important coproducts or byproducts. In placer deposits, potential source minerals for thorium include monazite and several thorium-bearing multiple-oxide minerals. In veins or lodes the principal thorium-bearing minerals are thorite, monazite, and uranothorianite, and less commonly allanite, brockite, and brannerite. Thorium-bearing pyrochlore is found in some carbonatites.

TYPES OF DEPOSITS

Thorium concentrations of possible economic interest occur in the following types of deposits: (1) Veins, (2) beach and stream placers and residual deposits, (3) deposits in sedimentary rocks—ancient placer deposits, thorium-bearing dolomite (as found in Canada), and conglomerates or quartzites enriched in thorium and in some places uranium (as at Elliot Lake, Ontario), and (4) concentrations in igneous and metamorphic rocks, mostly of low grade, which include carbonatite, fenite, dikes or layers of alkalic igneous rock, thorium-rich granite, pegma-

tite, pegmatitic migmatite, and thorium-rich zones in metamorphic rock.

VEINS

Three types of thorium veins are known. First are the unique monazite-apatite veins of South Africa that have been the principal producers, but are largely depleted. The second type comprises uranothorite or uranothorianite deposits in Malagasy and on Bokan Mountain, Alaska; these also are largely depleted. The third type consists of veins composed chiefly of fine-grained quartz, potassium feldspar, and iron oxide. The most abundant thorium mineral in these veins is thorite, but monazite, allanite, or brockite are common in some places. Veins of this type are known at 13 localities in the United States. The veins are from a few feet to 5,000 feet long and many are 1–2 feet thick. They occur in steeply dipping fractures that cut across the structure of the host rocks; many are brecciated. In many areas the veins are adjacent to alkalic complexes and carbonatites. The veins formed from highly mobile fluids at low temperatures, and hence may be as much at 20 miles from their probable source.

The grade of the veins is commonly erratic, but many contain an average of several tenths of a percent thorium. A few veins, such as those in the Wet Mountains, Colo. (Christman and others, 1959, p. 522 and 530), and at Hall Mountain, Idaho (Staatz, 1972, p. 247), may contain several percent thorium. The rare-earth content of the veins may equal or exceed the thorium content. Inasmuch as the grain size is small and the iron oxide may be abundant, separation of thorium minerals by standard physical methods is difficult.

PLACERS

In many countries, monazite is a common accessory mineral in placer deposits that were formed from the debris of metamorphic and granitic rocks. Many of these placer deposits are formed on active beaches, where the monazite and other heavy minerals are concentrated in a narrow belt along the shoreward facies. Many placer deposits are extensive; some are more than 10 miles long and one-quarter mile wide. Some placer deposits occur in partly indurated beach sediments that now lie landward of the active beaches.

In tropical areas, where weathering has been extensive and penetrated deeply, beach placers may contain more than 50 percent heavy minerals that consist chiefly of ilmenite or magnetite, although garnet, zircon, rutile, sillimanite, cassiterite, or monazite may also be sufficiently abundant to be economically important. The monazite, however, generally occurs in minor amounts compared to many of the other minerals. The ThO_2 content of monazite in these deposits is highly variable, and commonly ranges from 3.5 to 9.0 percent (Parker and Baroch, 1971, p. 67), but the ThO_2 content of the monazite from any one deposit or area is fairly constant.

Stream placers are smaller and tend to be less uniform in composition than beach placers, and therefore must be of higher unit value to be worked successfully. Monazite generally is the principal and only thorium mineral in these deposits, but other thorium minerals are found in a few places. The principal thorium mineral is euxenite in the placers at Bear Valley, Idaho, and uranothorite in the Hailey area, Idaho (Mackin and Schmidt, 1956).

DEPOSITS IN SEDIMENTARY ROCKS

Some sedimentary rocks consist chiefly of indurated placer sediments, such as those of fossil beach deposits. In some of these deposits, the sorting and concentration of the valuable minerals has been more complete than in others. In some of these deposits especially in sandstone and conglomerate, the heavy minerals tend to be dispersed, but even here they have been concentrated because the softer or more brittle minerals have been ground finer and carried farther away. Monazite is commonly the only thorium-bearing mineral found, but near Elliot Lake, Canada, it occurs with brannerite and uraninite (Roscoe and Steacy, 1958, p. 482). The latter two minerals, important sources of uranium, are found in conglomerates in ancient Precambrian rocks.

Indurated sedimentary rocks require grinding to liberate the thorium minerals—unless they contain an important coproduct, such as uranium, they are not likely to be mined until the less expensive unconsolidated placers are largely exhausted.

CONCENTRATIONS IN METAMORPHIC AND IGNEOUS ROCKS

Thorium minerals are found in some metamorphic and igneous rocks. Monazite is especially widespread in metamorphic rocks of garnet to sillimanite grade. In a few small areas, such as near Central City, Colo. (Young and Sims, 1961), and in southern Music Valley, California (Evans, 1964), monazite and xenotime are concentrated, but the deposits are too small to mine.

Thorium minerals are commonly associated with potassic igneous rocks, especially granitic and alkalic complexes. Also related to these igneous rocks are bodies of carbonatite, which commonly contain several valuable minerals. Thorium occurs in some such carbonatites; for example, it might be recov-

ered as a byproduct of rare-earth mining at Mountain Pass, Calif.; of niobium mining at Araxa, Brazil; or of copper mining at Palabora, South Africa.

Most granite contains an average of 0.0025 percent thorium, but granite with a greater content of thorium could be a potential low-grade resource. The Conway Granite underlies a large area in New Hampshire and, in addition to uranium, contains more than twice as much thorium as the average value already cited (Adams and others, 1962, p. 1903). The granites of the Tokovskii complex in the U.S.S.R. contain four times the average thorium content of granite (Filippov and Komlev, 1959, p. 541).

RESOURCES

IDENTIFIED RESOURCES

The resources of thorium are not well known, owing in part to the small demand in relation to available supply. The increased use of thorium for generating electricity, however, has stimulated interest in resources. Because the amount of byproduct ThO_2 recovered throughout the world in 1972 was more than sufficient to meet current needs, deposits in which thorium is the principal element cannot be mined at a profit.

The present known resources of ThO_2 in the United States as given in table 94 include resources recoverable as byproducts as well as both high- and low-grade nonbyproduct resources. The only minable reserves at present are some of the Atlantic Coast beach placers, where monazite is produced as a rather minor byproduct of titanium mining. Resources of beach placers along the Atlantic coast include 15,600 tons of ThO_2 estimated to be in monazite in the sands in Florida, on Hilton Head Island, S.C., and in some of the ancient beach placers near Folkston, Ga.

The United States has large resources (table 94) of thorium in relatively high-grade veins—those containing more than 0.1 percent ThO_2. The Wyoming and Michigan resources, which occur in detrital monazite in conglomerates, are too low-grade for recovery to be feasible until higher grade and easier-to-handle ores such as placers and veins have been depleted. These conglomerates are nonuraniferous, and thorium cannot be recovered from them as a byproduct as it can in the uraniferous conglomerates at Elliot Lake, Canada. A large potential source of thorium is in the low-grade deposit of granite near Conway, N.H. This granite, the Triassic or Jurassic Conway Granite which has an average grade of 0.0064 percent ThO_2, underlies an area of about 307 square miles (Adams and others, 1962, p. 1903), and could be mined at a cost of about $50–$100 per pound of ThO_2 (Brown and others, 1963, p. 6–11). More than half of the world's identified resources of thorium are in beach placers, principally in India (table 94). The total resources of thorium in beach placers are undoubtedly larger, inasmuch as in some countries, such as Brazil, Australia, and Malaysia, only part of the beach placers has been evaluated. Furthermore, present-day beach placers are being formed continually, and in some areas new placers may form several years after the old one has been worked out.

Carbonatites are also an important resource of thorium, containing more than one-sixth of the evaluated thorium resources potentially recoverable as a byproduct (table 94). Thorium can be recovered as a byproduct of copper and uranium mining at Palabora, South Africa, and of niobium and rare earths at Araxa, Brazil. About 40 percent of the known resources of thorium potentially recoverable primarily as a byproduct is in the uranium deposits in the Elliot Lake district in Canada. As these deposits are being actively mined for uranium, only a separate circuit need be added to the mill waste after the precipitation of the uranium in order to recover a thorium-rich concentrate.

The largest known resources are in Greenland, where several square miles of lujavrite, a variety of nepheline syenite, contains 200 ppm to several tenths percent thorium and a half to a quarter as much uranium. The cost of recovery of either element, however, would be high.

Although the identified resources of thorium are small compared to those of many other metals, they are large compared to the amounts of thorium used in the past. Known resources are about 10,000 times greater than the amount used in 1968. The general use of thorium in reactors would, however, greatly enlarge the demand for this element, hence the appraisal of potential resources becomes important.

HYPOTHETICAL AND SPECULATIVE RESOURCES

Beach placers have been and will continue to be major sources of thorium. Resources in some places will probably be increased as additional areas of known monazite-bearing sand are evaluated. Thus, a favorable area for finding new placers is below the water level, off present beaches, where seaward extensions of known placers could be mined under somewhat more difficult conditions. McKelvey (1968, p. 40) estimated the monazite content in undiscovered marginal offshore deposits on the U.S. continental shelf to be about 4 million tons. Even larger off-shore deposits probably occur in Australia, Brazil, and India.

TABLE 94.—*Identified thorium resources*

[Identified resources are specific, identified mineral deposits that may or may not be evaluated as to extent and grade, and whose contained minerals may or may not be profitably recoverable with existing technology and economic conditions]

Locality [1]	Type of deposit	Thousands of short tons ThO_2			Principal published reference
		Recoverable primarily as by-product or coproduct	Recoverable primarily for ThO_2 of grade—		
			>0.1 percent	<0.1 percent	
United States:					
Atlantic coast	Beach placer.	16	----	---	McCauley (1960, p. 1).
North and South Carolina	Fluviatile placer.	----	----	56	Overstreet, Theobald, and Whitlow (1959, p. 713–714).
Idaho and Montana	---do	2	----	38	
Lemhi Pass district, Idaho and Montana	Veins.	----	100.0	---	U.S. Atomic Energy Comm. (1969, p. 127).
Wet Mountains, Colo	---do	----	4.5	---	
Powderhorn district, Colo	---do	----	1.5	---	
Mountain Pass district, California	---do	----	.5	---	
---do	Carbonatite.	28	----	---	
Palmer area, Michigan	Conglomerate.	----	----	46	Olson and Overstreet (1964, p. 37).
Bald Mountain, Wyo	---do	----	----	2	Borrowman and Rosenbaum (1962, p. 2).
Total, United States		46	106.5	142	
Australia	Beach placers.	50	----	---	Griffith (1964, p. 106).
Brazil:					
Atlantic coast	---do	20	----	---	Stamper and Chin (1970, p. 685).
Morro de Ferro, Minas Gerais	Alkalic rock complex.	----	14.0	---	Wedow (1967, p. 30)
Araxa, Minas Gerais	Carbonatite.	130	----	---	Guimaraes (1957).
Canada: Elliot Lake, Ontario	Conglomerate.	[2] 580	----	---	Griffith and Roscoe (1964, p. 11).
Greenland: southwest part	Alkalic rock complex.	----	----	750	European Nuclear Energy Agency (1967, p. 13).
India; various areas, including Kerala, Bihar, West Bengal	Placers.	450	----	---	Bhola and others (1965, p. 93).
Kenya: Mrima Hill, Mombasa area	Carbonatite.	21	----	---	Davidson (1956, p. 206).
Korea	Fluviatile and beach placers.	6	----	---	Olson and Overstreet (1964, p. 32–33).
Malagasy Republic [1]: Fort Dauphin area	Beach placers.	10	----	---	Murdock (1963).
Malaysia	Placers.	20	----	---	Shortt (1970, p. 207).
Malawi	Fluviatile and beach placers.	----	----	10	Bowie (1959).
South Africa [1]: Palabora, Transvaal	Carbonatite.	75	----	---	Pike (1958, p. 94).
Uganda: Sukulu, Eastern Province	---do	2	----	---	Davidson (1956, p. 206).
United Arab Republic: Nile delta	Fluviatile and beach placer.	10	----	---	Higazy and Naguib (1958).
West Africa: Nigeria, Sierra Leone	Placers.	15	----	---	Bowie (1959).
Total world identified resources		1,435	120.5	902	

[1] Not shown, because of inadequate data, are resources in Argentina, Ceylon, parts of Malagasy Republic, Norway, South Africa (Steenkampskraal monazite veins), Uruguay, U.S.S.R., and several other countries.

[2] Includes some hypothetical resources, which are undiscovered mineral deposits, whether of recoverable or subeconomic grade, that are geologically predictable as existing in known districts.

Knowledge of certain factors in the formation and concentration of monazite can aid in the search for undiscovered placers. Monazite commonly forms by recrystallization during metamorphism, and the thorium content of the monazite increases with the grade of metamorphism (Overstreet, 1967). Monazite weathered from metamorphic rocks is concentrated in the near-shore sediments laid down in the ocean. If these sediments are raised above sea level and are in turn eroded, monazite may be reconcentrated. Beaches in which the monazite has gone through more than one cycle of erosion and deposition, in general, have greater concentrations of monazite than those that have gone through only one cycle. Furthermore, more monazite is freed from rocks where the enclosing minerals are thoroughly weathered—for example, in warm, humid climates. In arid climates the rocks do not weather as deeply, and in the far north the monazite in the sediments may be dispersed by glaciation. In the search for new monazite beaches, effort should be concentrated in areas in subtropical or tropical climates that have

high-grade metamorphic rocks inland and Tertiary or Cretaceous clastic rocks along the coastline.

Additional resources of thorium will also be found in vein deposits in areas that have not been thoroughly prospected because of lack of demand for thorium. Undiscovered resources exist both in known districts at untested depths (hypothetical resources), and in areas where no thorium deposits have yet been found (speculative resources). Districts containing vein deposits, such as Lemhi Pass, Idaho-Montana, Hall Mountain, Idaho, and the Wet Mountains, Colo., have had little subsurface exploration and parts of the areas are covered by thin Quaternary deposits. Exploration in these areas will undoubtedly discover many new deposits, and additional exploration at depth may well increase resources several times over those now known in veins. The origin of many thorium vein deposits is related to the formation of alkalic stocks and their associated carbonatites. Hence, prospecting within a radius of about 20 miles from known alkalic stocks well may locate new thorium vein districts.

PROSPECTING TECHNIQUES

Methods of prospecting for thorium vary according to type of deposit and other factors. The most useful methods rely on the radioactivity of thorium. Geiger and scintillation counters have been widely used in detection and appraisal of thorium deposits. Abnormal radioactivity can also be detected with a gamma-ray spectrometer, and the content of thorium, potassium, and uranium daughter products can be measured in a few minutes with this instrument.

Except for the radioactivity methods, thorium prospecting is carried out by traditional techniques of examination and sampling of favorable terrane. Panning for heavy minerals is particularly useful in areas where placer concentrations occur. Methods of exploration by panning and churn drilling of placer deposits in Idaho, North and South Carolina, and other States have been described by Kline (1952). Water sampling has not been used for thorium deposits because of the low solubility of thorium in ground water, lakes, and rivers. Sampling of stream sediments has been tested by Staatz, Bunker, and Bush (1971) in the Lemhi Pass district where its usefulness is quite limited.

Because of the limited market for thorium, very few deposits have been explored at depth by drilling or underground excavations. Radioactivity methods penetrate only a very thin surface layer, hence in most areas the extent and grade of deposits at depth are conjectural.

RESEARCH NEEDED ON DOMESTIC THORIUM RESOURCES

The United States will probably continue to obtain the greater part of its thorium needs, at least for the next few years, from foreign sources. Embargoes by several principal producing countries tend to diminish this supply greatly. These embargoes, coupled with the very likely large growth in demand, would shift some of the interest from foreign to domestic sources. The most easily available resources of thorium in the United States are beach placers in Florida and Georgia mined for their titanium content, but the monazite recoverable is limited not only by the size and grade of the deposits but by the demand for titanium.

A larger and still untapped U.S. resource is the thorium veins of the West. Complete reserve estimates are needed on the veins in each district (length, thickness, depth, and average grade). Information is needed on the relation of these veins to regional faulting and to alkalic intrusives and on their ages, mineralogy, total rare earth content, and on the relative distribution of the various rare earths to one another in the veins.

Small amounts of thorium also occur in carbonatites in the United States. Additional study of the mineralogy and chemistry of these deposits would help to determine the amount and recoverability of thorium, possibly as a byproduct of rare earths or niobium.

Definition of thorium-rich metallogenic provinces, by the grouping of deposits or districts and the thorium content of various rocks, should aid in outlining target areas for future prospecting.

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OIL AND GAS

By T. H. McCulloh

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ABSTRACT

Thermal "cracking" of part of the biogenic organic detritus interred in fine-grained subaqueous sediment releases hydrocarbon compounds that form petroleum and natural gas.

Rapid nearshore marine deposition favors accumulation and preservation of such sedimentary organic matter. Temperatures high enough for cracking to begin and compactional pressures great enough to actuate mechanisms of hydrocarbon expulsion and migration require basinal burial to depths of 1,500 feet or more. Wherever fluid hydrocarbons migrating toward the surface are interrupted and trapped, oil and gas reservoirs occur.

Organic carbon, hydrocarbons, and producible hydrocarbon accumulations are distributed extremely unevenly in the United States and the world. They are practically restricted to sedimentary rocks and are much more abundant in geologically young strata than in old. Producible hydrocarbons occur with greatest frequency and in greatest volume at depths shallower than 10,000 feet, and a very small percentage of all known accumulations contains a very large percentage of all proved reserves. A few regions (notably the Middle East) contain a disproportionate share of the world reserves.

All estimates of petroleum and natural gas resources depend upon prior exploration results and are unreliable. Changing economic incentives, technologic advances, enlarged prospecting areas, and creative thinking all increase exploration effectiveness.

INTRODUCTION

THE PROBLEM

What are the ultimate potential United States and world resources of petroleum and natural gas, both those discovered and those waiting to be found? Where are they? What part of them can be found and exploited economically? What fraction of the total was originally within the territorial limits of the United States? How much of that fraction lies beneath the continental shelves—and where? To what extent will the United States be dependent in the future on imported petroleum, and how can we be assured of an economical supply? What should be the national goal and policy toward encouraging domestic exploration on land and beneath the continental shelves? What part of our national research and investment capability should be devoted to programs aimed at utilizing coal resources or nuclear "fuels" more fully in the future in place of petroleum and natural gas? Should special incentives be provided to support conservative but eco-

nomically marginal operation of "stripper wells," of "tight gas reservoirs," of secondary recovery operations?

The answers to these questions, and myriads like them, are of the utmost concern or importance today to business leaders, industrialists, economists, politicians, international strategists, and military planners. To an important extent, the answers stem from geological, geophysical, and geostatistical research and investigations. Whether such questions are answered correctly or incorrectly, the life of every citizen living in the United States in the year 2000 will be affected profoundly by the actions that are being taken now on the basis of the answers available. The very long lead times required to discover and develop wholly new petroleum and natural gas reserves requires that planning be done now to fill needs anticipated or projected for the last decade of the 20th century (Hartley, 1969; Harvey, 1970; Moody, 1970). Even longer lead times are needed to plan, finance, and conduct research into new and improved methods of seeking the hard-to-find deposits of hydrocarbons that will be needed by future generations.

GEOLOGIC SETTING

Petroleum ("rock oil"). and natural gas ("earth gas") are mixtures or solutions of raw chemicals. They are natural fluids composed predominantly of compounds of hydrogen and carbon. The simplest of these compounds is methane, the principal constitutent of natural gases. More complex hydrocarbon compounds of higher molecular weights that have been identified as constituents of petroleum number in the many hundreds, but about half of the weight of average crude oil consists of light hydrocarbon compounds containing from three to 14 carbon atoms per molecule. Many semi-independent lines of evidence indicate that these natural hydrocarbon chemicals are of ultimately biological origin. The most compelling evidence is the overwhelmingly predominant tendency for both the fluid hydrocarbons and associated organic matter to occur in sedimentary rocks, especially in those of marine and lacustrine origin that were deposited rapidly in basins or depositional centers. Posthumous organic detritus interred in subaqueous sediment is the starting material from which these scarce and valuable fugitive raw chemicals were derived.

Hydrocarbon compounds are virtually ubiquitous in differing amounts at and near the surface of the earth and in the rocks and pore fluids beneath the surface. Small quantities occur in living protoplasm (from a few parts per million on a dry weight basis in most higher organized living matter to a few thousand parts per million in some plankton and microorganisms), mostly of compounds having 15 carbon atoms or more per molecule. Even in the atmosphere, trace amounts occur near biological sources, in coal mines, at oil and gas seepages, at some volcanogenic vents, and in association with dust particles. Small quantities make up part of the few milligrams of dissolved organic substances per liter of average sea water, and minute amounts occur in some meteorites and in a few places even within the crystals of coarse-grained igneous rocks. But by far the greatest proportion of the hydrocarbons in the earth occurs in sediments and sedimentary rocks.

Organic carbon and hydrocarbons are distributed extremely unevenly in the earth's sedimentary mantle. In Holocene sediments, they are generally most abundant in marine silt and clay deposited rapidly in basins or depressions on or at the edges of continental shelves. They decline in abundance as grain size increases and are least abundant in coarse-grained sediments. They are present even in nonmarine deposits, but at generally much lower levels, and are abundantly present there only in lacustrine deposits, especially those that are hypersaline.

The average content of organic carbon in Holocene marine clastic sediments of continental derivation was long ago recognized to be about 1.4 percent (Trask, 1937, p. 149; Trask, assisted by others, 1932, p. 249). Subsequent investigations confirm this as a rough approximation but also suggest that the complicating effects of basin size, continental shelf width, basin morphology, and hydrodynamic and hydrobiological features render any "average" figure of little use (compare for example, Emery, 1960, tables 12 and 27, and Bordovskiy, 1965, p. 37–44). Hydrocarbons are associated with the organic matter of Holocene marine sediments in the lipid (or "bitumen") fraction. According to Trask, assisted by others (1932), the mean "bitumen" content of such sediments is 0.06 percent, and the data of many authors show that the ether-extractable content of individual samples, although quite variable, is directly proportional to total organic carbon, therefore being generally highest in quickly buried pelitic sediments. These early findings of Trask have also been supported by subsequent investigations (Smith, 1956; Bordovskiy, 1965, p. 57–68) but with the addition of such important details as the facts that such "bitumens" consist of about 65 percent asphaltenes and about 10 percent oils (0.005 to 0.015 percent of dry sediment) and that

molecules having odd numbers of carbon atoms conspicuously predominate among the heavy normal paraffins (Bray and Evans, 1961).

The great bulk of the organic carbon that occurs in sedimentary rocks, like the total organic matter and most of the hydrocarbons, is disseminated in low concentrations through large rock volumes. On the basis of many tens of thousands of rock samples (Trask, 1937, p. 149; Trask and Patnode, 1942; Ronov, 1958; Hunt, 1962; Gehmen, 1962), the organic carbon contents of unmetamorphosed sedimentary rocks are known to range between a high of 1.77 percent (average) for coastal-marine shales of petroliferous regions and a low of 0.15 percent (average) for nonmarine carbonate rocks of nonpetroliferous areas. The data of Trask and Patnode (1942) and especially of Ronov (Ronov and others, 1965, p. 330; Ronov, 1968, fig. 7; 1958, figs. 1 and 2) show that the distribution of organic carbon in sedimentary rocks is not at all constant through geologic time. Instead, a long-term increase from very low concentrations in young Precambrian clay strata of the Russian Platform (0.08 percent organic carbon for 700-million-year-old Sinian strata) to high concentrations in Mesozoic and Cretaceous clays (0.41 percent organic carbon) is attributed by Ronov and his coworkers ". . . to the overall increase in the total mass of living substances in the biosphere." Major fluctuations in this long-term increase have been demonstrated (Ronov, 1958, table 2 and figs. 1 and 2) from data from the Russian Platform and the United States (Trask and Patnode, 1942). Figure 57 summarizes these data and emphasizes the remarkable parallelism between the Russian and the U.S. stratigraphic averages. Tappan and Loeblich (1970), calling attention to the worldwide contemporaneity of such geochemical fluctuations with important marine and terrestrial biologic events, suggested that changes in the quantitative distribution of marine phytoplankton are the fundamental causative link connecting such otherwise apparently unrelated correlations (see also House, 1963).

Knowledge about the uneven distribution of total organic carbon in sediments of different grain sizes and depositional environments and in sedimentary rocks of different regions and ages is both sketchy and problematic; but it is vastly more complete and satisfactory than knowledge about the hydrocarbon compound whose carbon forms but a minute part of the organic carbon. The relatively small quantities of hydrocarbon compounds, their mobility and physicochemical lability, and the relative newness of many of the analytical procedures and equipment

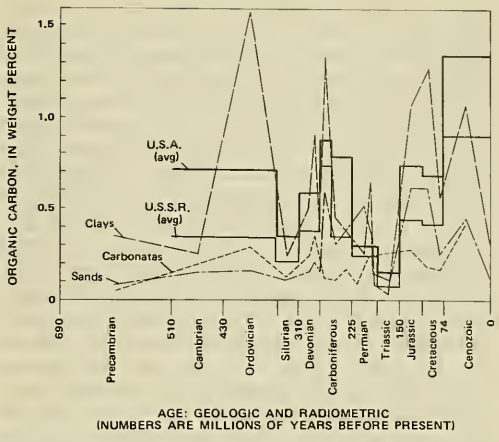

FIGURE 57.—Age-dependent variations in the average content of organic carbon in sedimentary rocks from the Russian Platform and the United States. Adapted from Ronov (1958, figs. 1 and 2).

needed for quick reliable quantitative determinations of most of them, combine with the enormous scope of the undertaking to be more conducive to ignorance than to knowledge.

Hydrocarbon compounds have been identified from some of the oldest Precambrian strata (3-billion-year-old Fig Tree shale of the Swaziland System, South Africa) and, among others, from unmetamorphosed carbonaceous middle Precambrian undoubted microfossiliferous chert (1.9-billion-year-old Gunflint Iron Formation, Ontario, Canada). However, critical investigations of the origins of these compounds (aromatic hydrocarbons in the older shale and normal alkanes and saturated and unsaturated fatty acids in the younger chert) indicate that the hydrocarbons are present because of contamination that possibly is quite recent. They are neither indigeneous nor syngenetic with the mainly indigenous carbonaceous materials (Hoering, 1967, p. 99–100; Abelson and Hare, 1968; Smith and others, 1970; Nagy, 1970). As Hoering (1967, p. 105) so clearly stated in his remarkably farsighted treatment of such problems of hydrocarbon contamination, "Vast quantities of geologically younger petroleums are a part of our present environment and can appear in unsuspected places."

However, the detection of chemically stable metalloporphyrins in an extract of 1.1-billion-year-old Nonesuch shale from northern Michigan (Barghoorn and others, 1965) points clearly to a biogenic origin for the organic matter from which this relic

of photosynthetic organisms was derived (Treibs, 1936; Orr and others, 1958; Dunning, 1963). Furthermore, the evolution of an impressive series of alkanes (methane through pentane) by low temperature pyrolysis from ether-insoluble organic matter (kerogen) extracted from this same stratum (Hoering, 1967, p. 97 and table 4) indicates that the seepage petroleum (first reported by White and Wright, 1954) from the White Pine Copper mine is almost certainly younger Precambrian in age, and the Nonesuch shale is its ancient source rock. Carbon isotope ratios from the soluble and the insoluble fractions of the Nonesuch organic matter are almost identical and diagnostically biosynthetic (Hoering, 1967, table 8) and further strengthen this conclusion. Negative results were reported by Hoering from his attempts to detect optical activity (rotation in the Nonesuch petroleum by ". . . a factor of 50 less than has been reported from Paleozoic petroleums.") The likelihood that polycyclic, saturated hydrocarbons are responsible for some of the optical rotation so characteristic of younger petroleums (Oakwood and others, 1952; Hills and others, 1970) and that sterols are precursors of such compounds takes on special interest in view of the fact that anaerobic organisms do not produce highly unsaturated fatty acids or sterols (Bloch, 1965).

Many other occurrences have been reported (Vassoyevich and others, 1971; Murray, 1965) of possible, probable, and undoubted Precambrian hydrocarbons from many localities in the world, but none is as thoroughly documented by pertinent observational and analytical detail as the occurrence in the Nonesuch shale. Of these other occurrences, the oldest that appears to be fairly certainly indigenous is 1.2 b.y. (saturated paraffinic compounds extracted from "Muhos shale" of the Jotnian series, Finland—Hoering, 1967, p. 98–100), and most are from youngest Precambrian rocks. Of further interest is the fact that only one undoubtedly Precambrian occurrence has resulted in commercial hydrocarbon production; that of gas, condensate, and oil from the late Proterozoic multizone Markovo field in the Irkutsk part of the western Siberian Angara-Tunguska basin (Vassoyevich and others, 1971, p. 412–413). *Commercial* petroleum and natural gas are almost exclusively products of sedimentary rocks deposited during only the last one-eighth to one-fourth of the earth's history, that part during which an atmosphere rich in oxygen prevailed and during which complex multicellular organisms developed. Carbon is the stuff of life!

The evidence has been summarized which indicates that hydrocarbon compounds are quite scarce in rocks of Precambrian age, even those relatively rich in organic carbon and kerogen, and that fluid hydrocarbons (commercially producible or not) are extremely rare in such strata and are restricted thus far to rocks of late Proterozoic age. It is self evident, then, that most of the earth's hydrocarbons must occur in rocks of Phanerozoic age and in Holocene sediment (plus the biosphere and hydrosphere). Qualitatively at least, the long-term increase in organic carbon concentrations of clays of the Russian Platform appears to be paralleled by a worldwide increase in hydrocarbon concentrations from late Precambrian to Mesozoic and Tertiary rocks. Whether these relationships result primarily from temporal variations in the primary productivity of the ancient biosphere, or whether other time-dependent factors intervene and override, such as diagenetic (metamorphic) modifications of the hydrocarbon precursors in sedimentary organic matter or erosional, structural, or thermal events that reduce sedimentary rock volume, rock porosity, or the effectiveness of hydrocarbon traps, remains to be examined quantitatively Quantitative data are needed regarding variations in the hydrocarbon concentrations of Phanerozoic rocks as a function of geologic age and depth of burial (thermal history). Unfortunately, only a start has been made toward that goal, and that only coincidentally as a result of commercial prospecting for petroleum and natural gas.

PRODUCIBLE HYDROCARBON ASSESSMENT

Compared with the tremendous efforts that have been expended in the industrial search for commercially producible fluid hydrocarbons (especially in the United States and elsewhere in North America), the previously mentioned efforts to assess the organic carbon contents of sedimentary rocks, impressive and valuable as they are, are completely overshadowed. In the United States alone, more than 2,222,300 wells, totalling 7 billion feet of hole in all (R. F. Meyer, oral commun., Jan. 25, 1973), have been drilled in the search for petroleum and natural gas. Most of those holes were located after much deliberation, on the basis of substantial scientific and technical data expertly evaluated. They were drilled either to exploit hydrocarbon reservoirs already known to exist from prior exploratory drilling, or as "wildcats" with the specific objective of evaluating scientific hypotheses advanced by technical advisors who suggested the possibility of finding abnormally rich concentrations of hydrocarbons; concentrations large enough and sufficiently energized that part of the crude chemicals could be pro-

duced profitably to the surface. The results of such endeavors can be regarded in a sense as a rock-hydrocarbon assessment of sorts; not of the total hydrocarbon content of sedimentary rocks of all types, but a sampling of that fraction of the total organic matter which was mobilized sufficiently at one time or another to have been expelled from its source stratum and enabled to migrate through permeable pathways toward regions of lowered pressure (ultimately the atmosphere), and to be trapped along the way to accumulate more-or-less temporarily in a *producible* and *findable* reservoir.

The industrial search for commercial hydrocarbons has not been a random search, except locally to a minor degree. Therefore, the results of the search cannot be treated in all regards as data gathered randomly or according to some consciously designed sampling scheme. For example, rocks at great depth have been prospected much less thoroughly than rocks at shallower depths because of economic considerations. (Shallow reservoirs have been easier to find and cheaper to exploit, and shallow discoveries provided sufficient production to serve the needs of the United States until recently.) Similarly, reservoirs associated with structural traps, especially anticlinal traps, have been subject to a more diligent search than a variety of other more subtly-trapped accumulations because exploration techniques thus far available are best suited to structural mapping. In attempting to use the statistical data resulting from the search for petroleum and natural gas, limitations (or sampling bias) such as these should be kept in mind.

Limitations of another sort should be explicitly recognized. To a very large extent, the most reliably useful data available from drilling for hydrocarbons are the records of the amounts and kinds of fluids produced. These have been measured. Less reliable and much more difficult to interpret are *estimates* of the producible *"proved reserves,"* or of the amounts of crude oil or natural gas *"initially in place"* in a reservoir or field. Such estimates depend not only upon interpretations of a variety of difficult geologic and engineering measurements, but also in part upon assessments of variable economic factors. "Cumulative production" plus "proved reserves" constitute that fraction that is known or judged to be economically and physically extractable of the hydrocarbons "initially in place" in a reservoir. Statistical data from the United States indicate that currently an average of 30 percent of the "oil in place" and 80 percent of the "gas in place" are economically extractable (Moore, 1970a, p. 133; Elkins, 1971). Keeping these limitations in mind, let us examine the data available from drilling and production.

Cumulative production of crude oil through 1971 was 264 billion barrels for the world and 97 billion barrels from the United States. Proved reserves for the world and the United States are 632 and 38 [1] billion barrels, respectively (see fig. 61). World and U.S. cumulative production for natural gas are 620 and 415 trillion cubic feet, respectively, and proved reserves are 1,725 and 279 trillion cubic feet, respectively. When dissected and examined in detail, these figures reveal that the known commercially producible hydrocarbons in the world and the United States are distributed extremely unevenly, but according to the following general and important regularities.

Of overriding importance is the fact that a very large percentage of the total oil (and gas) occurs in a very small percentage of all known accumulations. More than 85 percent of the world's hydrocarbon production plus reserves occur in less than 5 percent (238 fields) of all producing accumulations. Even more remarkable, 65 percent of the hydrocarbons (petroleum and gas) occurs in slightly over 1 percent of all fields—the 55 "supergiants" (a billion barrels or a trillion cubic feet or more; Halbouty and others, 1970; Klemme, 1971), and an astounding 15 percent occurs in only two immense accumulations in the Middle East region (Ghawar field in Saudi Arabia and Burgan field in Kuwait). In smaller areas similar conclusions hold. For example, Halbouty (1968) showed that of the 22,898 oil and gas fields in the United States as of January 1, 1968, only 308 (1.33 percent) will yield about 60 percent of the presently estimated ultimately producible hydrocarbons. The importance of this tendency was first clearly stated by Heald (1950, p. 15). "If we are concerned with our future, we will study the record of major discoveries, the distribution of major fields, the geological conditions under which they exist, and will strive to recognize the areas wherein major discoveries are now unlikely or impossible as well as those in which major fields may be."

Almost equal in importance to the tendency for a few accumulations to contain most of the producible hydrocarbons is the tendency for those hydrocarbons to occur with greatest frequency and abundance in geologically young rocks. Halbouty and others (1970) provide the most recent data that show how the world's known oil and gas are dis-

[1] Estimate by American Petroleum Institute. S. P. Schweinfurth, U.S. Geological Survey, estimates U.S. proved reserves at 45 billion barrels (oral commun., Feb. 9, 1973).

tributed according to the age of the reservoir rocks. Their data (fig. 58) show 29 percent to be Cenozoic (0–74 m.y.b.p. (million years before present)), 57 percent to be Mesozoic (74–200 m.y.b.p.), 8 percent to be Permian (200–225 m.y.b.p.), and less than 6 percent to be pre-Permian in age. For comparison, Radchenko (1968, table 50) gives, on the basis of "data up to 1960," 49.4, 21.5, 4.7, and 24.4, respectively, as the percentages of total world cumulative production for the same four stratigraphic intervals. Current estimates for the United States yield percentages that are significantly different from either set of world percentages (fig. 58). The percentages of known producible hydrocarbons from U.S. reservoir rocks of both Cenozoic and Paleozoic ages are much higher than the world percentages, and that for Mesozoic reservoirs are much lower. These differences reflect the strong influence of the vast reserves in the Middle East (more than 62 percent of the world reserves), a large part of which are in reservoirs of Mesozoic age. Considering only production and reserves from "giant" fields outside the Persian Gulf region, Tertiary, Mesozoic, and Paleozoic rocks contain 40, 39, and 21 percent, respectively, of the total producible reserves. As offshore exploration and development in the United States continue, the U.S. percentages for Cenozoic and Mesozoic hydrocarbons will doubtless increase at

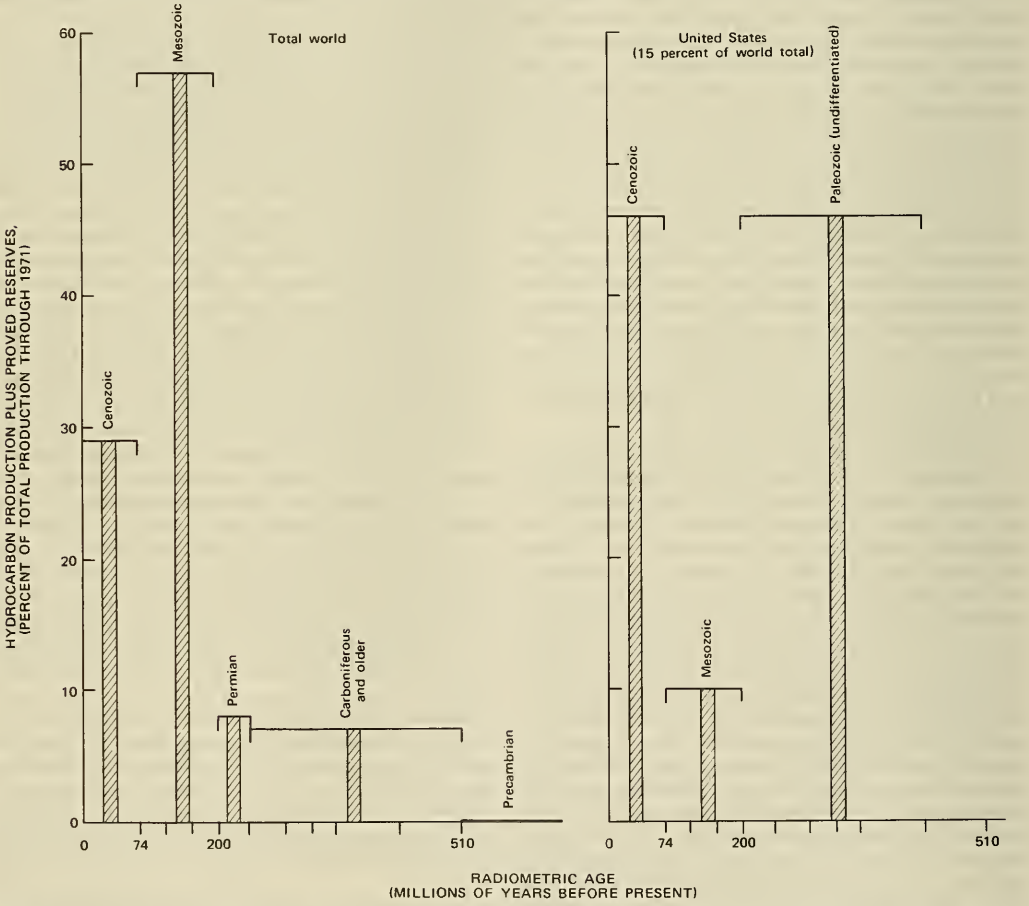

FIGURE 58.—Age-dependent variations in produced and proven reserves of oil and gas for the United States and the world.

the expense of the percentage of Paleozoic oil and gas because of the volumetric predominance of Cenozoic and Mesozoic marine strata beneath all U.S. continental shelves (Weeks, 1971, p. 99; Gilluly and others, 1970, especially p. 368). The fivefold larger average volume of geologically very young pools than pools in most Mesozoic and Paleozoic rocks (Hopkins, 1950, fig. 4) is of importance in relation to this fact.

Not only the relative amounts, but also to some degree the chemical and physical characteristics of crude oils depend systematically upon the geologic age of the rocks in which they occur. Statistical comparisons of crude oil properties from U.S. fields (and a few Venezuelan and Canadian fields) over a wide range of geologic ages and depths (Hopkins, 1950, fig. 1; McNab and others, 1952; Biederman, 1965) show beyond doubt that petroleums of low density occur with greater frequency in Paleozoic rocks and that those of high density make up the greatest proportion of crudes in Tertiary rocks. Furthermore, the older crude oils show a clear tendency toward a higher percentage content of low molecular weight fractions and a low content of oxygen- and nitrogen-containing materials. The young crude oils contain appreciable amounts of oxygen- and nitrogen-containing compounds, more like the organic precursors from which they evolved. Evidently, a progressive time-dependent evolution or maturation occurs from dense crude oils rich in large cyclic compounds, forming early and tending to occur in young sedimentary rocks, to less dense crude oils composed of more paraffinic compounds of lower molecular weights and more characteristic of older rocks. Perhaps this is why 50 percent of the hydrocarbons reservoired in U.S. "giant" fields of Paleozoic age are gas (Halbouty and others, 1970, p. 532). However, hydrocarbon composition is influenced strongly not only by the length of time it has had to mature, but also by the depth (temperature) to which it has been subjected, and to some extent by compositional characteristics of the source materials (Martin and others, 1963; Dean and Whitehead, 1964; Hedberg, 1968); thus, simplified interpretations of compositional data are generally risky and equivocal.

The influence of depth of occurrence on hydrocarbon composition has long been recognized (White, 1915; Barton, 1934; Hopkins, 1950; McNab and others, 1952; Biederman, 1965; Landes, 1967). Hudson (1963, p. 133) emphatically underscored the empirical fact that commercial quantities of crude oil do not occur in the United States at depths greater than about 20,000 feet and are *unlikely* to occur deeper than about 16,000 feet. Phase relations among the compounds of petroleum and natural gas indicate that only the simple hydrocarbon compounds in a gaseous phase can exist at temperatures and pressures prevalent at depths of about 20,000 feet or more (Halbouty and others, 1970, p. 533). At shallower depths (and lower temperatures) than those beyond which hydrocarbons do not persist as liquid petroleums, other depth-dependent variations in petroleum composition occur. Specific gravity of deep crude oil is statistically lower than that of shallow oil of the same age, and the deeper crude oil contains higher proportions of lower molecular weight compounds (McNab and others, 1952, p. 2558–2560). Thus, it appears clear that the higher temperatures imposed by great depth of burial affect petroleum maturation and hydrocarbon alteration in much the same way as do extended periods of time. This in turn poses several questions of fundamental and practical importance, such as: Through what depth range are earth temperatures appropriate to cause thermal disintegration of the disseminated organic matter in sedimentary rocks to form liquid and gaseous hydrocarbon compounds? How do such thermal disintegration processes affect the residual organic matter (both the kerogen and the solvent-soluble fraction) left behind dispersed through the rock? By what mechanisms do newly-formed fluid hydrocarbons migrate from minute interstitial capillary openings in fine-grained rocks into units permeable enough to serve as reservoir rocks? What is the fate of relatively immature dense petroleum, containing minor proportions of low molecular weight compounds, if subjected to elevated temperatures attendant upon subsidence and deep burial of an initially shallow accumulation? A very large amount of work has been done in the search for answers to these questions and still only partial answers exist. Let us defer further consideration of the questions until more of the pertinent facts have been summarized.

Just as petroleum quality (composition) is distinctively dependent upon reservoir depth so, for discovered hydrocarbons, is petroleum *quantity*. In his pioneer treatment of the exceptional importance of exceptionally large hydrocarbon accumulations, Heald (1950, p. 19–20) explicitly recognized that most petroleum and gas occurs in reservoirs at depths shallower than 10,000 feet. He stated, "If history is a dependable guide, the existence of producible oil or gas at a depth of not more than 6,500 feet, is almost a prerequisite if a major field is to be opened." On the basis of worldwide production statistics available through 1960, Radchenko (1965,

p. 213 of 1968 translation) calculated the following percentages of petroleum production volume according to depth ranges for all fields.

Depth (meters)	Depth (feet)	Production (percent of total volume)
<500	<1,640	6.9
500–1,000	1,640–3,280	32.3
1,000–1,500	3,280–4,920	26.1
>1,500	>4,920	34.7

Virtually two-thirds of all oil produced up to 1960 came from reservoirs shallower than 1,500 meters. For the 45 North American oil fields recognized as containing ultimate recoverable reserves of 500 million barrels or more (Moody and others, 1970, p. 11 and fig. 11) and comprising "35 percent of the continent's total ultimate recovery," the average reservoir depth peaks sharply at about 4,000 feet (averaged on the basis of volume of ultimately recoverable reserves), and almost no reservoirs lie below 14,000 feet. These and like statistics, based on a great deal of exploratory drilling and production, lead one to conclude that most, if not all, commercially producible crude oil reservoirs occur at depths shallower than 20,000 feet and that more than one-half of the ultimate petroleum production of the world will come from depths shallower than 10,000 feet (and possibly from depths shallower than 5,000 feet).

The reasons for such findings obviously are of the greatest possible practical importance, and they are to be found above all in the fact that total porosities of clastic sedimentary rocks, including reservoir sandstones, diminish regularly with increasing depth because of gravitational consolidation following burial (Athy, 1930; Hedberg, 1936; Dallmus, 1958; Maxwell, 1964; Atwater and Miller, 1965; McCulloh, 1967). "This decrease in porosity . . . is the most important single factor controlling the amount of oil or gas in place per unit volume of sandstone reservoir rock" in the Tertiary strata of the United States Gulf Coast region (Atwater and Miller, 1965). Lithology, geologic age, and variations in geothermal regime are some of the complicating factors, but notwithstanding these, porosities of most clastic rocks approach limiting values close to 5 percent at depths of 10,000 to 20,000 feet, whereas average resorvoir porosities in excess of 30 percent are possible (and commonplace in young sedimentary rocks) at depths shallower than 4,000 feet (McCulloh, 1967, fig. 4). Shallow depths, high sandstone porosities, large reservoir volumes, and large hydrocarbon reserves (and production) all go together. Porosities of reservoir rocks of other lithologies follow more complicated rules, and it would be of considerable interest to determine whether or not petroleum from other than sandstone reservoir rocks predominates in the fraction produced from depths greater than 10,000 feet.

The data have been reviewed which show that petroleum and natural gas are distributed extremely unevenly through the earth's sedimentary mantle. Most of the commercially producible volumes of hydrocarbons that have been discovered to date occur in Tertiary and Mesozoic marine strata; more than half occurs in Mesozoic and Tertiary reservoirs of the Persian Gulf region. Between one-half and two-thirds of the petroleum occurs in reservoirs less than 10,000 feet deep, and essentially all commercial oil production is from depths shallower than 20,000 feet. Crude petroleum composition depends statistically upon depth and geologic age and only to a minor extent on original depositional environment. Shallow or young oil tends to be dense and chemically complex and exhibits strong similarities to altered biogenic precursors found in young nonlithified sediments. Deep or old oil tends to be light, chemically simple, and has a high content of low molecular weight paraffinic compounds. Reservoirs at depths of 20,000 feet and more contain gas only, although there is a gradual downward transition from deep accumulations of crude oil rich in dissolved "gas" and gasoline fractions, through reservoirs containing natural gas liquids (NGL), to natural gas reservoirs in which only minor quantities of higher molecular weight compounds occur. If meaningful prognostic predictions are to be made of where and in what amounts producible accumulations of petroleum and natural gas may occur, one must recognize not only that the distribution of fluid hydrocarbons in sedimentary rocks and basins is extremely uneven (although subject to certain broad general patterns), but a substantial understanding of the underlying physical and chemical reasons for their uneven distribution is needed. We must have an understanding of the nature of the processes by which organic detritus interred in sediment is transformed to protopetroleum and thence to fluid hydrocarbons capable of migration, and of the chemical and physical processes by which such mobilized hydrocarbons are expelled from source rocks and trapped during their migrations to form commercial accumulations.

FLUID HYDROCARBONS FROM SEDIMENTARY ORGANIC DETRITUS

Laboratory pyrolysis experiments (Hunt, 1962; Abelson, 1964) and extraction experiments (Welte, 1966) performed on kerogen-bearing rock indicate

that saturated paraffins and aromatic hydrocarbons are released from kerogen when heated and are removable in solution in hot oil-field brine. Field observations of the stages in the progressive diagenesis and metamorphism of coals and particulate coaly matter contained in sediments buried to different depths, and from which hydrocarbons have been expelled, provide one means for gauging that potentially fluid hydrocarbons are released during natural thermal diagenetic transformations of organic matter (White, 1915; Teichmüller, 1958; Brooks, 1970) through a wide range of depths, from probably less than 5,000 feet to almost certainly more than 15,000 feet, depending upon local geothermal gradients and duration of maturation conditions. Such conclusions have been reached independently by comparing presumably related reservoir and source rock hydrocarbon compositions (Baker, E. G., 1962) coupled with observations of depth-dependent variations in ratios of hydrocarbon carbon to total noncarbonate organic carbon (Philippi, 1957 and 1965). They are in excellent quantitative agreement also with some results of studies of depth-dependent variations in gross composition of dispersed organic and bituminous matter in nonreservoir strata (Larskaya and Zhabrev, 1964; Neruchev, 1964). Together with interpretations of systematic relations observed among the distinctive carbon isotopic compositions of natural organic substances (including natural gases, petroleum gases, specific petroleum fractions, whole petroleums, solid hydrocarbons, asphaltenes and tars, kerogen, coals, and unaltered biogenic materials), these results suggest that progressive low-temperature decomposition or thermal cracking of protopetroleum, composed importantly of high molecular weight compounds derived in substantial part from plant lipids, accounts for all the chemical relationships thus far observed (Silverman and Epstein, 1958; Silverman, 1964; Frank and Sackett, 1968; Vinogradov and Galimov, 1970; among others). Further research on the kerogen fraction of fine-grained interstitial organic matter of sedimentary rocks is badly needed to help clarify in very young and very old sedimentary rocks both the shallow and deep limits of depth (temperature) at which diagenesis makes parents of organic precursors of fluid hydrocarbons. Such research would probably be facilitated by applying electron spin resonance and infrared spectroscopic techniques in the search for additional reliable compositional data, especially C/H ratios (Marchand and others, 1969), that the coal studies have suggested may be important temperature indices. More research is also needed on the observable effects of later thermal alteration or destruction of petroleum which accumulated during an earlier episode of hydrocarbon release and migration in a reservoir at shallow or moderate depth. Sufficient evidence is available now to say that even mature petroleum rich in paraffinic compounds of relatively low molecular weight undergoes further thermal cracking if subjected to sufficiently high temperatures (Evans and others, 1971, p. 151–153) and would break down ultimately to highly fugacious methane on the one hand and solid graphitic carbon on the other. These are also the ultimate products of thermal degradation of the insoluble organic residues that remain in nonreservoir strata, or for that matter of coal.

The metalloporphyrins of many crude oils are not only evidence of a biological origin for the petroleums, but they also set a limit on the temperature at which the transformation from sedimentary organic detritus to petroleum constituents occurs. Green porphyrin pigments, decay derivatives of chlorophyll, are commonly present in fine-grained marine and lake sediments. Through a series of hydrogenation and decarboxylation steps, sediment porphyrins may be diagenetically altered to metalloporphyrins containing vanadium or nickel such as occur in petroleum. The thermal stability of such compounds is such that they do not survive at temperatures above 200°C (Welte, 1965, p. 2257), and they thus set an upper limit on the temperature of the transformation process responsible for their presence in a petroleum. Unfortunately, there is no certainty that all constituents of a crude oil originated at the same time or place or at the same temperature. It would be a matter of some interest, however, to attempt to determine the depth of disappearance of metalloporphyrins from crude oils of widely differing depths (but confined to particular stratigraphic horizons), as a means of determining whether or not the various crude oils represent fractions of one or more phases of petroleum genesis.

PETROLEUM MIGRATION AND ENTRAPMENT

Once formed, fluid hydrocarbons must be expelled from the capillary pores of the fine-grained organic-rich source rocks before migration, entrapment, and accumulation can occur in shallower permeable reservoir rocks. The expulsion mechanism is not well understood, although it probably is complex. Expulsion may occur simply because of differential capillary pressure exerted because of two-phase fluid saturation of adjacent rocks of differing capillary sizes (Washburne, 1915, especially p. 832–834;

Hubbert, 1953, p. 1979; Gussow, 1954, p. 821). Alternatively, hydrocarbons may dissolve in hot aqueous pore waters under pressure, either directly (Uspenskii, 1962, p. 1161; McAuliffe, 1966; Meinchein, 1959) or with the solubilizing assistance of organic "soaps" (Baker, D. R., 1962). In either case, porosity reduction because of gravitational compaction through continuing subsidence and loading (sedimentation) tends to express the pore waters and their dissolved or emulsified hydrocarbons from the finer grained and less permeable source rocks into coarser grained and more permeable (and porous) carrier and reservoir beds (Athy, 1930; Hedberg, 1936; Uspenskii, 1962, p. 1163; Philipp and others, 1963; Magara, 1969). Thermal recrystallization and dehydration (diagenesis or eometamorphism of clays or other hydrous mineral phases) in source rocks depressed to depths of thousands of meters provide further opportunities for flushing of dissolved or suspended hydrocarbons (Burst, 1969; Magara, 1969) into reservoir rocks or carrier beds. The underground temperature gradient in sediments and sedimentary rocks favors the "primary migration" of oil from source beds by stimulating dehydration reactions in the clay minerals which tend to decrease mineral adsorption capabilities in deeper levels (Snarskiy, 1962), by providing a temperature-dependent adsorption gradient favoring movement of hydrocarbons from regions of higher to regions of lower temperature (Watts, 1963), by stimulating upward diffusion along the temperature gradient (Watts, 1963; Witherspoon and Saraf, 1964), and by establishing local inter-pore or inter-bed pressure gradients because of the large volumetric expansion of hydrocarbons, as compared to water or brine, subjected to a temperature increase (McCulloh, 1967).

In a subsiding depositional basin, a number of processes all work hand in hand. These include physical depression of petroleum source rocks, augmentation of rock temperature, chemical transformation of organic precursors to hydrocarbon constituents of petroleum and natural gas, loading and gravitational rock compaction with attendant reduction of pore space, and the establishment of temperature and pressure gradients along which expressed pore water and entrained or diffused mobile hydrocarbons tend to migrate toward the surface. The greater the depth, the higher the temperature and the simpler (molecularly) the mobile (liquid or gaseous) hydrocarbon phases that are in thermal equilibrium with the environment. The greater the depth, the higher also the confining pressure, and the greater the tendency of thermally energized (and potentially greatly expandable) mobile hydrocarbon phases to escape to lower pressure regions. No wonder that for many years courts of law in the United States classed oil and gas as "fugacious minerals" or "minerals ferae naturae"—wild beast minerals (Hedberg, 1971, p. 15).

"Primary migration" apparently can begin when suitable source rocks have been depressed to a depth of 500–600 meters or more (Philipp and others, 1963; Welte, 1965, p. 2263), although considerable evidence suggests that about 1 kilometer may be a more general upper limit (Welte, 1972, p. 122). During basin subsidence, an oil source rock can undergo progressive geochemical development during which an evolutionary series of hydrocarbons are generated under gradually higher temperature conditions. "Primary migration" of these hydrocarbons proceeds at least as long as gravitational compaction continues to reduce source rock porosity and diagenetic alteration of clays continues to release unbound water for expulsion. "Primary migration" merges into "secondary migration," in which hydrocarbons expelled from fine-grained source rocks begin to move more freely through coarser-grained carrier beds (or fractures) having physical characteristics of reservoir rocks. If permeable avenues exist to permit the expressed fluids egress directly to the surface, the hydrocarbons escape more-or-less directly. If, on the other hand, the carrier beds provide no direct or unimpeded avenue of escape to the atmosphere, the ultimate dumping ground for all mobilized hydrocarbons, trapping occurs in regions of minimum pressure along potential paths toward the surface, and petroleum or natural gas accumulations are formed. Throughout the migration process, no matter what the mechanism, the tendency for the migrating fluids is to attain the most stable state (generally the lowest level of potential energy) possible. This tendency is consistent with the expulsion of fluid hydrocarbons from fine-grained source rocks and with their migration across strata or through carrier beds or fractures toward the surface from deep regions of higher temperature and greater confining pressure. The tendency is also consistent with aggregation of hydrocarbons into accumulations in local regions of lower pressure where they displace all but films of the water in the rock pores; with long-continued slow leakage of hydrocarbons (selectively the low-molecular weight compounds) from large accumulations; and with the well-known propensity for oil and gas wells to "blow out" or "go wild," releasing their "minerals ferae naturae" abruptly (and with potential destructiveness) to the atmosphere.

Entrapment of fluid hydrocarbons occurs wherever their tendency to escape to the atmosphere is interrupted or significantly impeded by any impervious or relatively impermeable barrier having a geometry suitable to hydrocarbon aggregation and accumulation, rather than to diversion. Both static (lithologic or mineralogic) and dynamic (hydrodynamic) barriers are effective, and an almost infinite variety of reservoir "traps" (McCullough, 1934) occur, the classical example of which, the anticlinal dome, consists of an upfolded (inverted cup-shaped) stratum of a porous permeable reservoir rock capped by a layer of shale, anhydrite, or other rock relatively impermeable to penetration by or transmission of large hydrocarbon molecules. Petroleum or natural gas constituents migrating gravitationally up-dip along natural escape routes through the permeable stratum are diverted toward the locus of minimum fluid pressure at the dome crest where they tend to be trapped and aggregate to form an anticlinal "pool" or reservoir. No attempt is made here to describe the myriads of other kinds of "traps" that have been recognized (Levorsen, 1954, p. 138–282). Any region of porous and permeable rock is a "trap" if it is connected more or less directly with pathways along which hydrocarbon fluids migrate (or once migrated), either in aqueous solution or as discrete intergranular filaments, droplets, globules, or slugs, and if it is enveloped or sealed up-dip (downstream from a potential viewpoint) by a barrier that prohibits hydrocarbon escape. When a petroleum or natural gas accumulation is opened by drilling, the fugacious hydrocarbon contents are permitted to resume their journey to the atmosphere. There they are ultimately oxidized, one way or another, to carbon dioxide and water, thereby bringing to completion the cycle that began (in some instances hundreds of millions of years earlier) with photosynthetic fixation of carbon in the organic compounds of living plants. The ultimate fate of most hydrocarbon accumulations that are not opened by drilling is to very slowly leak their contents to the surface (hence the historical importance to petroleum exploration of surface seepages, and the continuing efforts to understand surface geochemical anomalies and to develop practical geochemical prospecting methods (Pirson, 1970, p. 208–239; Armstrong and Heemstra, 1972)). Other accumulations are opened by erosion at the surface following tectonic uplift, oxidized gradually through the actions of oxygenated waters circulating from the surface, or degraded by bacterial decay (World Oil, 1972). Doubtless the relative scarcity of geologically ancient petroleums is partly due to their fugitive nature in relation to the abundant opportunities for escape through geologic time. Possibly the fivefold to fifteenfold greater average volume of Pliocene than older reservoirs in the United States (Hopkins, 1950, fig. 4) is thus explainable.

Figure 59 is an attempt to portray diagrammatically, but semiquantitatively, a few of the more conspicuous or diagnostic steps in the evolution of fluid hydrocarbons (such as comprise petroleum and natural gas) from organic debris interred in sediment and subjected to progressively higher temperatures upon burial in a subsiding basin.

PETROLEUM AND NATURAL GAS RESOURCES

Oil and gas fields are effective hydrocarbon traps that have been discovered through human resourcefulness. In general, those traps that have *been* discovered are those that are conspicuous (from the viewpoint of the host of exploration techniques that have been invented and employed), are of very large size, or are located in regions that have undergone thorough prospecting. Remaining to be discovered are innumerable small reservoirs, large reservoirs that are inconspicuous (when subjected to the exploration techniques available), and traps of all sizes in regions that have not yet been prospected thoroughly or at all.

Who can say what the undiscovered resources of petroleum and natural gas are of the world or the United States? What are the incentives for seeking still more sophisticated and effective methods of exploring for undiscovered traps? In considering these questions one must keep in mind that not all subsurface hydrocarbon accumulations are *worth* finding. For every accumulation that can be found and produced *economically*, there are doubtless *many* accumulations of such small size that the volumes of hydrocarbons producible are insufficient to repay the costs of finding (including as they do the very great costs of drilling and completing the well, the high costs of exploration, and of all other efforts associated with such a technologic exercise). Under these circumstances it is obvious that small shifts in the supply/demand ratio for petroleum and natural gas bring about substantial shifts in numbers of accumulations and volumes of hydrocarbons from the paramarginal to the recoverable category. Similar effects are brought about by incremental improvements in exploration or exploitation technology. One must also keep in mind in considering these questions that the purposeful discovery of fluid hydrocarbons is a human endeavor, and one in which people have not been long engaged. Very large areas of the earth, especially portions of the

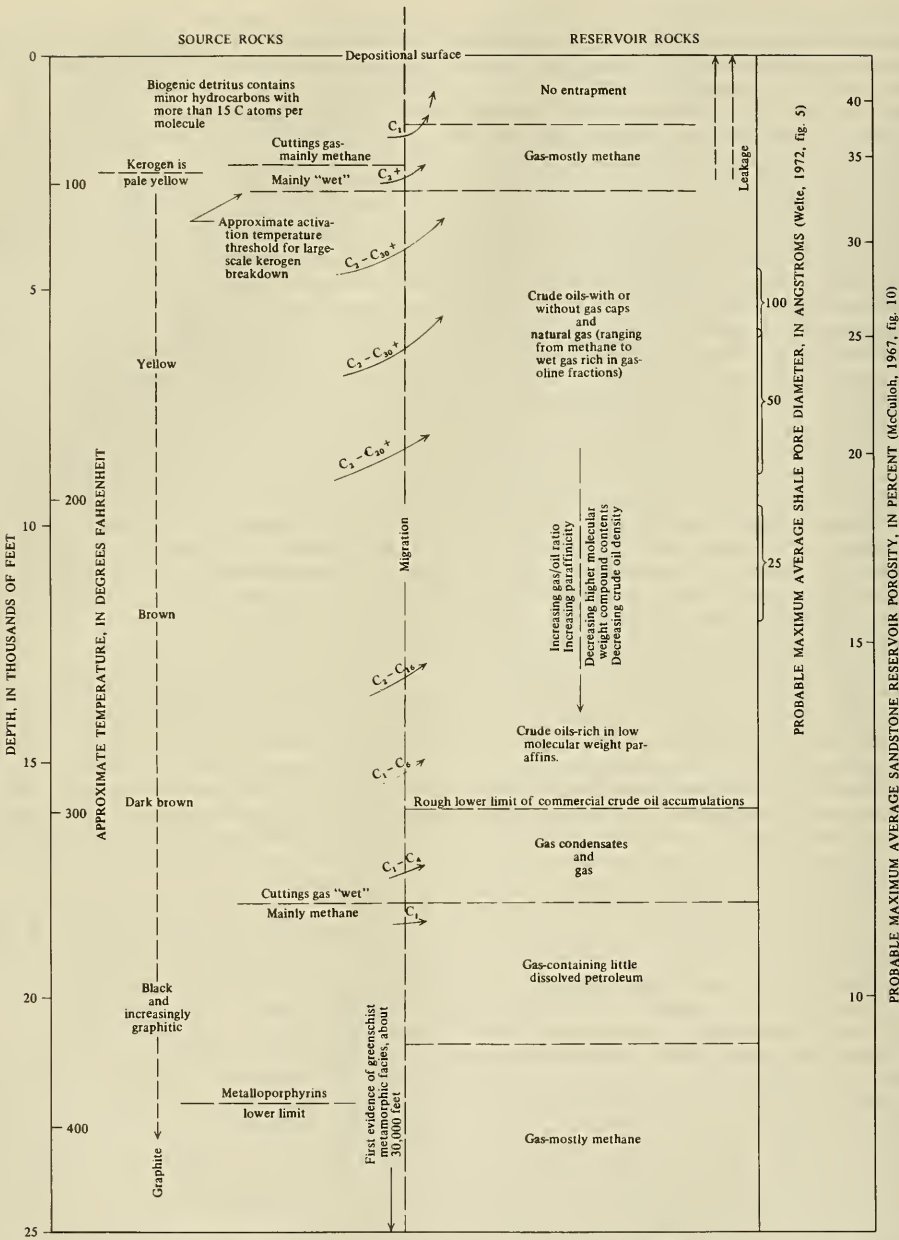

FIGURE 59.—Selected diagnostic and critical steps in the genesis and migration of petroleum and natural gas from sedimentary organic matter.

seabed, have yet to be adequately explored geologically (Weeks, 1971). Our techniques for identifying hydrocarbon traps, or even those areas that especially favor hydrocarbon accumulation, are very imperfect. On both counts, the results of petroleum exploration to date serve as an inadequate baseline upon which to project results of future exploration. Nevertheless, the results of past exploration provide the most reliable *single* guide that we have.

A decision must be made at the outset as to what will be an acceptable minimal sample unit or baseline if one is to attempt to use results of past exploration as a guide to future projections. For example, if one were to estimate the ultimate recoverable hydrocarbon resources of the United States on the basis of the productivity per square mile of surface area (or per cubic mile of sedimentary rock volume) of *either* the immensely productive Los Angeles Basin or the totally unproductive Imperial Basin, both Cenozoic basins of Southern California, the results in *each* case would be grossly in error. In the same way, estimations for unexplored regions would almost certainly be in error if the regional historical statistical data from either the aberrantly rich sedimentary areas or volumes of the Middle East or the exceptionally impoverished ones of Italy and the Adriatic Sea were to be used as guides. Out of ignorance and limited capability, one is tempted in such efforts to select the base unit to be an area as thoroughly explored and as large and diverse as possible, thereby hoping that an average of such extreme results as those from the Los Angeles and the Imperial Basins will somehow result and give a more meaningful blend. As a practical matter, one works with what is available, recognizing as he does that a fruitful field for further research awaits significant attack, and knowing that one thing needed is a sound measure of the frequency distribution of hydrocarbon productivity per unit of rock volume for a large enough number of depositional basins to provide a population curve representative for the world. There are few "Los Angeles Basins" in the world, and probably not many "Imperial Basins." Somewhere between these two extremes is the peak of a geologically composite population curve statistically applicable to totally unexplored basins and applicable with measured discrimination to geophysically analyzed basins or those only partly explored by drilling.

The conterminous United States ("lower 48"), because of its political and economic unity, its comparatively long and intensive history of petroleum exploration and exploitation, its relatively large size (5.3 percent of the continental area of the earth), its large volume of Phanerozoic rocks (estimated to be 60×10^6 km^3 by Gilluly and others (1970)), and its great geological diversity provides ". . . the most meaningful statistical sample for appraising possible ultimate potential" (Hendricks, 1965, p. 3). By starting with the quantity of petroleum found in the conterminous United States to the year 1961 and "the fraction of the potentially productive rocks that [had] been explored to [that] date," and by estimating the incidence of oil in the unexplored fraction ". . . as determined by comparison with the explored part," Hendricks arrived at an estimate of 1,600 billion barrels of oil originally in place for the "lower 48." He estimated further (p. 9) that a total of 1,000 billion of those barrels could be found if economic incentives were sufficient to stimulate additional thorough but profitable exploration, and that 400 billion barrels would be ultimately recoverable (of which 68 billion barrels had been produced through 1961, and 97 billion today). By contrast, starting with the same basic historical records and data, but using a method of mathematical analysis that is in his words intrinsically ". . . comparatively insensitive to error in the estimates of [ultimate cumulative production] . . . ," Hubbert in a series of papers (1956, 1962, 1966, 1967) concluded that the amount of ultimately recoverable petroleum in the United States is between 150 billion barrels for the conterminous states and about 200 billion barrels for the entire continental United States (including Alaska and the outer continental shelves). Hubbert's method is one of integral logistic curve fitting. It is related only statistically to rocks and geologic parameters, and to those only through a variety of economic and technologic factors. Supposing that human beings will be doing in the future as they have in the past, so far as petroleum exploration is concerned both technologically and from an investment viewpoint, Hubbert's approach is unassailable.

Hendricks was neither the only nor the first person to attempt to estimate undiscovered petroleum resources of the United States through an analysis of unexplored rocks based on analogy with historical results in explored areas. Twenty-three years earlier, Pratt (1942) published estimates of the ultimately discoverable and (presumably) producible petroleum resources of the United States and the world of 100 billion and 500 billion barrels, respectively. The Pratt figures came from estimates made by Eugene Stebinger and L. G. Weeks ". . . based on studies . . . made of the records of past discoveries and of the nature and extent of sedimentary basins over the

earth, which had yielded or appeared likely to yield oil" (Pratt, 1951, p. 9). De Golyer (1951, p. 9) criticized the Stebinger-Weeks-Pratt methods and assumptions in the following terms, "any hypothesis of equal expectation of minable oil by volume or area of sediments over large areas presupposes that the effects of all these processes will average about the same or, in case of inequalities that they will compensate." Of the figures themselves, De Golyer wrote, "They may be too high. They may be too low. I do not know. I am inclined to think that Pratt's original estimate of 100 billion bbl for the United States may be too low even if we add 13 billion bbl for the continental shelves . . . ." Inasmuch as cumulative production for the United States is today above 97 billion barrels, with 38 billion barrels more already categorized as "proved reserves" capable of economic extraction under current technology, the Stebinger-Weeks-Pratt estimation of 1942 was obviously an underestimation. The comparative success of a subsequent basically similar partial projection (Hopkins, 1950) leads one to ask, can we tell at this time that Hendrick's 1965 estimation of 400 billion barrels is an *overestimation*?

Although Hubbert's predictive (or projective) analytical procedure and results are perhaps more widely publicized than others, he is by no means the only scientist to have applied this method. Arps, Mortada, and Smith (1970) and Moore (1970a, b), provide examples of predictions made recently using similar mathematical analytical techniques which give somewhat divergent results; 165 billion barrels of "proved ultimate recovery discovered" (Arps and others, 1970, fig. 4) or 353 billion barrels (or 60 percent recoverable of 587 billion barrels of oil originally in place in the United States are predicted as discoverable; Moore, 1970a, fig. F-1). Does Moore know something that Hubbert does not to cause his projection to be so much higher (353 billion versus 200 billion barrels; or versus 165 billion in the case of Arps)? I think not. The projective techniques employed are all probably equally sound and the same basic data were entered into each projection. There is simply enough latitude in the method that such divergent results all lie within the range of valid results. More importantly, these divergences are a measure of the adequacy of the projective baseline, which is no doubt subject to further evolutionary change as economic incentives enlarge, as competitive pressures force improvements in conservative efficiency, and as technologic advances permit improved and expanded exploration (greater ability to discover smaller and less conspicuous traps and to exploit a larger part of the resource base and a larger part of the prospective rocks). Speaking of the annual world oil discovery rate in a similar context, Warmen (1971, p. 97) wrote, "for a curve with such violent fluctuations, it is not possible to carry out meaningful mathematical analysis." Needless to say, future changes in the baseline will inevitably be enlargements.

For the sake of easy comparison at a glance, all of the more authoritative estimates of future and ultimately producible petroleum for the United States have been brought together in figure 60 and plotted as a function of their date of publication. Plotted also is the gross curve of production plus cumulative discoveries. The reader will note that the many more or less independent projections show a great deal of scatter (divergences such as those among the projections of Arps, Hubbert, and Moore), and that they tend to grow with the passage of time in a fashion that more-or-less parallels the growth of the curve of cumulative production plus reserves. Both the scatter and the tendency to grow are meaningful. They reflect the fact that the area under consideration has not remained constant through time—new producing regions and areas have been brought into the picture through combinations of business enterprise, economic pressures of many sorts, technologic advances, and exploitation effectiveness. There is considerable room for continuation of this evolutionary advancement—in *all* respects. Much of the United States continental shelf is unexplored. Who can say at this time that another "Los Angeles Basin" doesn't wait for discovery and exploitation beneath the waters of the Southern California Borderland (Emery, 1960)? Who knows that there is *not* another "Middle East," for example, beneath the continental margin off the southern Atlantic coast of the United States, with another "Ghawar" accumulation (the largest single oilfield yet discovered in the world) containing another "75 billion barrels of producible reserves" (Arabian American Oil Company, 1959; Halbouty and others, 1970)? The onshore-offshore region south of Cape Hatteras has much in common geologically with the onshore-offshore region of Saudi Arabia, including a very thick section of structurally simple sedimentary rocks of the same ages and similar lithologies beneath a very large area. Prior to discovery by the drill and subsequent development, Ghawar field was *not* a particularly conspicuous prospect or structure, either from surface geologic mapping or geophysical interpretation (Arabian American Oil Company, 1959, especially p. 437 and p. 440–443). Does anyone know that

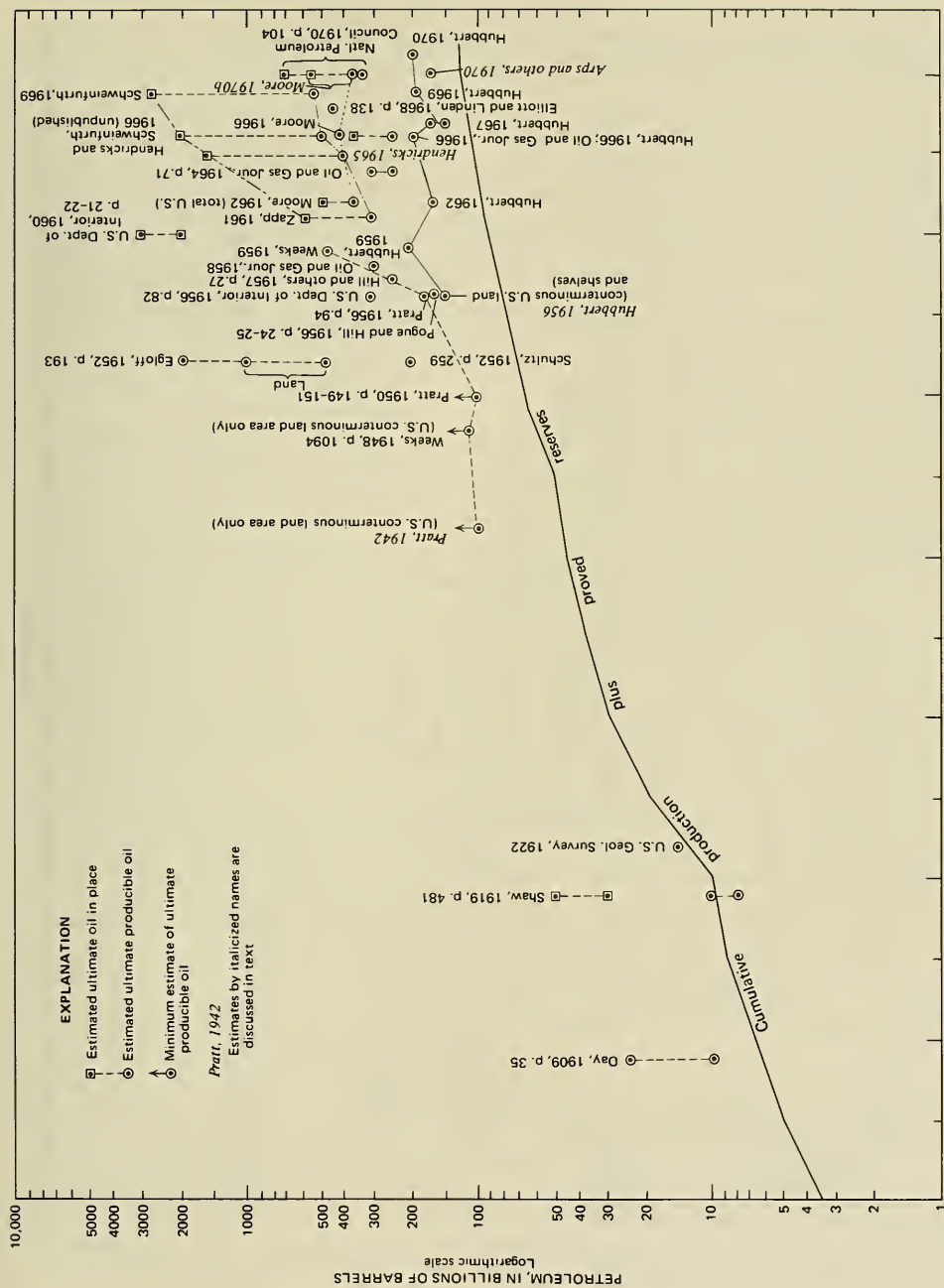

FIGURE 60.—Estimates of ultimate producible oil resources (and ultimate oil in place) of the United States, in relation to records of cumulative production plus proved reserves from 1900 through 1972.

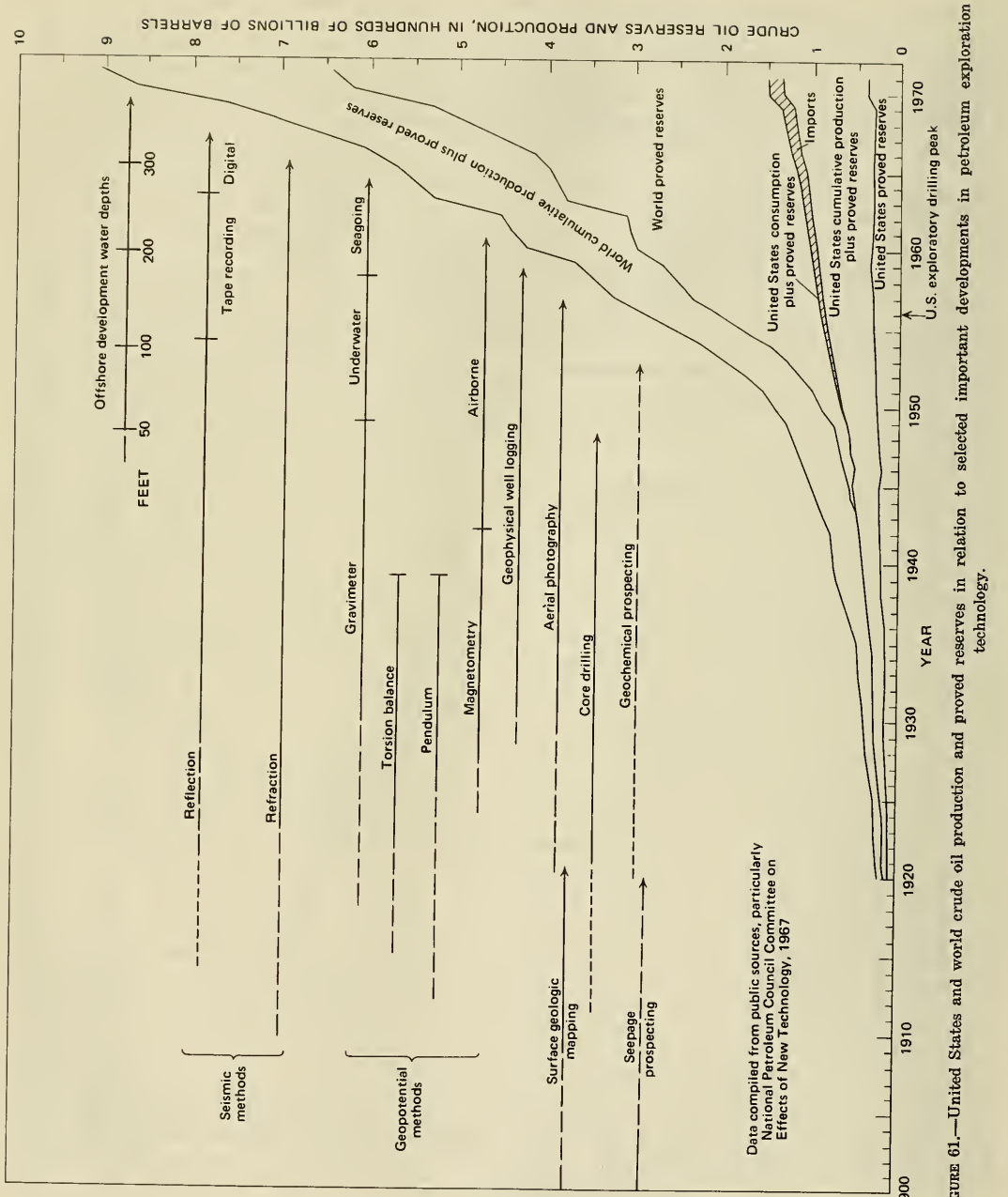

FIGURE 61.—United States and world crude oil production and proved reserves in relation to selected important developments in petroleum exploration technology.

another such inconspicuous "supergiant" does not lie beneath the Blake Plateau, or someplace else within the territorial limits of the United States? Although it is extremely difficult to envision circumstances which would make the United States ever again economically self-sufficient in oil and gas (see fig. 61), until we *know* that the last accumulation is discovered, should we trust the estimates of future producible oil, no matter how elegantly prepared or firmly stated? To discover petroleum and new petroleum provinces requires an open mind, a desire to explore, a positive and adventurous attitude, a gambling spirit, and a will to win. Last but far from least, although only the drill bit can finally prove the presence of oil, "oil must be sought first of all in our minds" (Pratt, 1942, p. 49).

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OIL SHALE

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ABSTRACT OF CONCLUSIONS

Oil shale, a fine-grained sedimentary rock containing insoluble organic matter that yields substantial amounts of oil by destructive distillation, occurs in large volumes throughout the United States and the world, and constitutes an enormous resources of oil. Identified resources of shale oil in the United States total about 2 trillion barrels of oil in shale that yields an average of 15 or more gallons of oil per ton, most of which is in the lacustrine rocks of the Eocene Green River Formation of Colorado, Utah, and Wyoming. Although no oil is being produced from oil shale in the United States, it seems likely that oil from high-yield shales will be needed in the near future to supplement other sources of energy. It is estimated that 0.42 trillion barrels of oil are in oil shale that yields 30 or more gallons of oil per ton, 85 percent of which is in western Colorado. Minerals locally associated with the rich oil shale may yield recoverable sodium carbonate, sodium bicarbonate, or aluminum.

Marine black shales occur in many parts of the United States and form an immense, but low-grade resource of shale oil. The better parts of these deposits generally yield only 10–15 gallons of oil per ton, but hydrogenation or similar techniques may increase the yield by 50 to 100 percent. Another widespread resource of shale oil may be the carbonaceous shales associated with coal beds. The total resources of shale oil to depths of 20,000 feet may total 26 trillion barrels in low-yield shales and 1.3 trillion barrels in high-yield shales.

INTRODUCTION

Oil shale is a fine-grained sedimentary rock containing organic matter that has the property of yielding substantial amounts of oil when heated in a closed retort (destructive distillation) but that is mostly insoluble in ordinary petroleum solvents. The United States has tremendous quantities of oil shade, principally in the Green River Formation in Colorado, Utah, and Wyoming. These three States contain identified resources of about 1.8 trillion barrels of oil in oil shale that yields an average of 15 or more gallons per ton. However, no oil-shale venture has been a commercial success in the United States in the last 100 years, despite the fact that other countries of the world have for many years burned oil shale as a fuel, or have produced oil or combustible gas from the shale. The principal reason for the lack of success is the abundant supplies of lower cost oil, gas, and coal that this country has developed. The rising demand for energy, however, may soon require the development of this abundant energy resource to supplement the dwindling supplies of other fossil fuels.

Duncan and Swanson (1965, p. 5) have estimated that about 400 million barrels of oil have been produced from oil shale in foreign countries prior to

1961, principally in Scotland, Estonia (U.S.S.R.), and Manchuria (China). Oil-shale deposits in France, Sweden, Germany, Spain, South Africa, and Australia have also been mined on a modest scale, and a new shale-oil operation is scheduled to begin in 1972 in Brazil.

In the United States, experiments in the production of oil and gas from oil shale have been conducted since 1850. Most early experiments were brief, ineffective efforts, but since 1944 pilot plants have been intermittently operated either by the U.S. Bureau of Mines (1944–56) or by private industry (1957–72) in the western Colorado oil-shale deposits. These pilot plants retorted oil shale that had been mined underground by conventional methods. In 1966, the U.S. Bureau of Mines estimated the cost of producing shale oil by this method at about $3 a barrel (Schramm, 1970, p. 192). In 1970, the National Petroleum Council (1972) also evaluated this method and estimated that each barrel of oil with a heat value of 5.4 million Btu would cost between $4.30 and $5.30 at the plant site. This estimate assumed a plant producing 100,000 barrels of oil a day (initial investment of $500 million) that used only the richer, more accessible oil shale (oil shale yielding 30–35 gallons of oil per ton, in zones more than 30 feet thick, within 1,500 ft of the surface). This cost compares unfavorably with the present price of crude oil, which is about $3.50 a barrel. It is probable, however, that the value of coproducts of shale oil, such as aluminum or sodium bicarbonate, or advancements in technology, or increases in the price of crude oil, will make shale oil competitive with crude oil in the near future.

The possibility of heating the oil shale underground and pumping the oil to surface (in situ retorting) has been investigated by private industry in western Colorado, and by the U.S. Bureau of Mines in southwest Wyoming (Schramm, 1970, p. 188). Many technical problems remain to be solved, but this method holds promise as a way to obtain the oil with little harm to the environment.

Synthetic gas can be produced from oil shale, but the cost of converting the organic matter to high-quality gas suitable for mixing with natural pipeline gas would appear to be greater per unit of contained energy. For example, it would cost $0.50 per million Btu to convert oil to gas.

OIL-SHALE DEPOSITS IN THE UNITED STATES

Oil shale occurs in many parts of the country in rocks ranging in age from Ordovician to Tertiary. Oil-shale deposits can be divided into three types—shale in lacustrine rocks, marine shales, and the shales associated with coal beds.

LACUSTRINE OIL-SHALE DEPOSITS

The principal oil-shale deposit of lacustrine origin is in the Green River Formation of Eocene age, which underlies about 17,000 square miles in Colorado, Utah, and Wyoming. Other small lacustrine deposits of Tertiary age containing oil shale have been reported in the intermontane basins of Montana, Nevada, Idaho, and California, but they remain unexplored.

The Green River Formation consists of oil shale interbedded with varying amounts of tuff, siltstone, sandstone, claystone, and locally with halite, trona, or nahcolite. The formation ranges in maximum thickness from a few feet to several thousand feet and intertongues laterally with the predominantly fluvial beds of the Wasatch Formation. The Green River Formation was originally deposited principally from two large Eocene lakes, one lying south of the Uinta Mountains and the other lying north and east. It is now preserved in seven basins—the Uinta Basin in Utah, the Piceance Creek and Sand Wash basins in Colorado, and the Green River, Great Divide, Washakie, and Fossil basins of Wyoming.

In the Piceance Creek deposit (Donnell and Blair, 1970; Donnell, 1961), the Parachute Creek Member of the Green River contains up to 2,000 feet of oil shale in alternating rich and lean beds. Some of these rich beds are very persistent; the Mahogany zone, for example, underlies more than 2,000 square miles in Colorado and Utah. The oil shale is thickest and richest in the north-central part of the Piceance Creek basin, where it also contains nodules, lenses, and beds of nahcolite ($NaHCO_3$) and halite (NaCl), and disseminated crystals of dawsonite [$NaAl(OH_2)CO_3$]. Nahcolite is potentially valuable as a source of sodium carbonate or sodium bicarbonate, and dawsonite as a source of aluminum. Toward the margins of the basin, the oil-shale sequence becomes progressively thinner and leaner, intertonguing with sandstone and siltstone.

In the Uinta Basin (Cashion, 1967), the Green River Formation is similar to that in the Piceance Creek basin, but the oil-shale sequence is thinner and leaner and does not contain significant amounts of saline minerals. In the Green River Basin, oil shale occurs in thin, but widespread units in the Tipton Shale, Wilkins Peak, and Laney Members of the Green River (Culbertson, 1972; Bradley, 1964). The Wilkins Peak Member locally contains thick beds of trona ($Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$) and halite, and disseminated crystals of shortite ($Na_2CO_3 \cdot 2CaCO_3$),

and other saline minerals, as well as thin zones of uraniferous phosphate, but the oil-shale beds in this sequence are so thin that they rarely constitute a resource where the trona and halite predominate. In the Washakie basin the richest oil shale is in the Laney Member of the Green River Formation (Roehler, 1969). The Wilkins Peak Member here is free of saline minerals and has been replaced in part by fluvial beds of the Wasatch Formation. The Tipton Shale Member is widespread, but available data indicate that its oil shale is lean.

In the Great Divide and Sand Wash basins, the Green River Formation is similar to that of the Washakie basin, but the oil shales are generally low grade. In the Fossil basin the Green River Formation was presumably deposited from a small lake separate from the main Green River lakes. The oil-shale sequence is thin and mostly low grade.

The oil shale of the Green River Formation is a dense, tough marlstone that is generally well laminated and ranges in color from tan to dark brown or olive-brown to brownish black. According to Bradley (1970, p. 985), the organic fraction is derived from "microscopic algae, and other microorganisms, that grew and accumulated in the central parts of large, shallow lakes that existed under a sub-tropical climate," and from "wind-blown, or water borne, pollens and waxy spores." The inorganic fraction consists predominantly of dolomite and calcite with varying amounts of quartz, feldspar, analcime, clay, and pyrite. The mineralogy and the variation in mineral composition of the oil shale in the Piceance Creek basin, Colorado, are described in detail by Brobst and Tucker (1973).

The sites of deposition of the oil shale were very flat. The lakes were large in area and the relatively shallow water ranged from fresh to highly alkaline. The surrounding highlands contributed clastic sediment to the margins of the lake, but during most of their history little or none of the clastic material was carried into the central part of the lakes. Conditions were such that algae grew abundantly on the surface of the lake, and their remains were preserved in the bottom sediments.

The basins sank slowly, and at irregular rates, causing the centers of deposition of oil shale to shift during Eocene time. In general, the areas were tectonically quiescent during deposition and for millions of years after the sediments were buried. Subsequently, uplift caused local tilting and erosion of these beds.

MARINE BLACK SHALE DEPOSITS

Black shale deposits of marine origin which underlie large areas in most of the United States consist of two main types. The platform-type marine black shales were formed in shallow seas on continental platforms where circulation of water near the sea floor was restricted. Characteristically, the platform shales may be several hundred feet thick, but the oil-shale zones are thin and persistent, ranging in thickness from a few feet to a few tens of feet (Duncan, 1967, p. 661). Although few of them have a high oil yield, they underlie such large areas throughout the world that their resources of shale oil are larger than that of any other type of deposit. Geosynclinal marine shales were formed in subsiding geosynclinal basins, and are associated with limestone, phosphate rock, and chert in assemblages much thicker than the platform type. Some deposits of this type, such as Miocene shales in California, yield significant amounts of oil.

The organic matter, which gives marine black shales their characteristic color, contains relatively little hydrogen, and therefore only a small percent of the organic matter converts to oil. According to Swanson (1960, p. 28), the organic matter is of two types: sapropelic (derived from algae, spore, pollen, etc.) and humic (derived from cellulose, lignin, and analogous woody parts). The inorganic fraction predominantly consists of quartz and clay minerals, although some shales contain carbonate. Many shales also contain small amounts of uranium, vanadium, and other metals, and phosphate.

A well-known example of the platform-type shale is the marine black shale of Late Devonian and Early Mississippian age that underlies more than 250,000 square miles in Eastern and Central United States. It is known principally as the Chattanooga Shale in the Central United States, but the names New Albany, Ohio, Antrim, Mountain Glen, and Woodford Shales refer to approximate stratigraphic equivalents elsewhere of the Chattanooga Shale. The black shale generally ranges from 0 to 100 feet in thickness, its average oil yield is about 5 gallons per ton of shale, and its average uranium content is 0.003 percent (Swanson, 1960, p. 7).

SHALES ASSOCIATED WITH COAL BEDS

Carbonaceous shales associated with coal beds are of two types: thin persistent beds deposited in a shallow marine environment and beds deposited in a swampy, nonmarine environment that are limited in extent and exhibit considerable lateral variation in organic content. In the Appalachian coal province, the Pennsylvanian rocks contain mostly nonmarine carbonaceous shales that have been reported to yield from 1 to 100 gallons of oil per ton, but most yield

less than 10 gallons of oil per ton. The richest beds —the cannel shales—are thin and of small extent. In the Interior coal province, the Pennsylvanian rocks contain numerous marine shales, persistent across thousands of square miles, Swanson (1960, p. 16) reported that about 40 distinct shale units occur in eastern Kansas and northeastern Oklahoma, but most of them are thin and yield 5–10 gallons of oil per ton. In Illinois, the oil yield of 114 samples from 30 marine shales ranged from 0 to 40 gallons of oil per ton, but 88 percent yielded less than 15 gallons of oil per ton.

RESOURCES

IDENTIFIED AND HYPOTHETICAL RESOURCES OF SHALE OIL

Identified shale-oil resources are those deposits for which sufficient data are available to establish the magnitude and oil yield within reasonable limits. Hypothetical resources are resources in possible extensions of identified deposits or in nearby deposits, in which the approximate magnitude of the oil-shale deposit is known, but whose oil yield is inferred from scant evidence.

GREEN RIVER FORMATION

The minimum thickness and grade of oil shale used by the U.S. Geological Survey in classifying public lands as valuable for oil shale of the Green River Formation is about equal to a sequence 15 feet thick, yielding an average of 15 gallons of oil per ton, but sequences yielding as little as 10 gallons per ton are included when computing the average yield of a thick sequence of oil shale. On this basis, the identified resources of the Green River Formation in Colorado, Utah, and Wyoming are estimated to total 1.8 trillion barrels of oil (table 95). Most of these identified resources (1.2 trillion barrels) are contained in the Piceance Creek basin of Colorado (Donnell, 1964; Donnell and Blair, 1970). The Uinta Basin of Utah is estimated to contain about 0.32 trillion barrels of oil (Cashion, 1964), and recent core data indicate that the Green River and Washakie basins of Wyoming together contain a similar amount.

Apparently none of these resources can be considered as economically recoverable now. However, a modest increase in the price of oil may make oil shale yielding an average of 30 or more gallons of oil per ton competitive with crude oil, so resources of this grade were calculated. Resources in high-grade shale, in zones more than 100 feet thick, total 418 billion barrels of oil (table 95), or nearly one-quarter of the identified resources of 1.8 trillion barrels. The major part of these high-grade resources (355 billion bbl) is in the Piceance Creek basin of Colorado; the remainder is in the eastern part of the Uinta Basin of Utah (50 billion) and in the southeastern part of the Green River Basin of Wyoming (13 billion). About 80 percent of these resources (325 billion) has been well evaluated by core drilling; the remainder is based on data which are sparse, or less reliable. Because conservative estimates of thickness and grade were used in areas where data were sparse, it is possible that the drilling of more core holes will require an upward revision of these resource figures.

TABLE 95.—*Shale-oil resources of the United States, in billions of barrels, by grade (oil yield) of oil shale*

[All resource figures except those for the Green River Formation are adapted from Duncan and Swanson, 1965, table 2; Ne, not estimated]

Deposit	Identified[1]		Hypothetical[2]		Speculative[3]	
	25–100 gal/ton	10–25 gal/ton	25–100 gal/ton	10–25 gal/ton	25–100 gal/ton	10–25 gal/ton
Green River Formation, Colorado, Utah, and Wyoming	[4] 418	1,400	50	600	----	----
Chattanooga Shale and equivalent formations, Central and Eastern United States	----	200	----	800	----	----
Marine shale, Alaska	Small	Small	250	200	----	----
Other shale deposits	----	Small	Ne	Ne	600	23,000
Total	[4] 418	1,600	300	1,600	600	23,000

[1] Identified resources: Specific, identified mineral deposits that may or may not be evaluated as to extent and grade, and whose contained minerals may or may not be profitably recoverable with existing technology and economic conditions.

[2] Hypothetical resources: Undiscovered mineral deposits, whether of recoverable or subeconomic grade, that are geologically predictable as existing in known districts.

[3] Speculative resources: Undiscovered mineral deposits, whether of recoverable or subeconomic grade, that may exist in unknown districts or in unrecognized or unconventional form.

[4] The 25–100 gal/ton category is considered virtually equivalent to the category "average of 30 or more gallons per ton"

The hypothetical resources of the Green River Formation are estimated to total about 650 billion barrels of oil, of which perhaps 50 billion barrels are in oil shales yielding 25–100 gallons of oil per ton.

The synthetic-gas potential of oil shales of the Green River Formation has been investigated by the Institute of Gas Technology. Their data indicate that by using different processing methods, high-quality synthetic gas could be produced at the rate of 100 cubic feet of gas for each gallon of shale oil that could be produced by a conventional retort, or 4,200 cubic feet for each barrel of shale oil. Thus, the Green River Formation could be the source of an enormous amount of gas, instead of oil, if so desired.

CHATTANOOGA SHALE AND EQUIVALENT FORMATIONS

Most of the marine black shales in the United States yield so little oil by conventional retorting (1–15 gallons of oil per ton) that it is difficult to consider them an economical resource of oil even for the distant future on this basis alone. However, many of the marine black shales have a high organic con-

tent, and as a result 10-gallon-per-ton shale, when treated by alternative methods such as hydrogenation or synthetic gas in a retort, can be made to yield 15–20 gallons of light oil per ton, or alternatively 1,700–2,600 cubic feet of high-quality synthetic gas. A minimum thickness and grade of 5 feet of shale yielding an average of 10 gallons of oil per ton by conventional retort was adopted by Duncan and Swanson (1965, p. 13) for computing oil shale resources. The identified resources of 200 billion barrels of oil (table 95) are in formations of Devonian and Mississippian age in the Central and Eastern United States. (See Duncan and Swanson, 1965, fig. 2.) They include resources in the central part of the eastern Highland Rim of Tennessee, where the Gassaway Member of the Chattanooga Shale averages 15 feet in thickness, yields an average of 10 gallons of oil per ton, and contains an average of 0.006 percent uranium (Conant and Stansfield, 1968). Areas of New Albany Shale in Indiana and Kentucky include black shale zones 20–100 feet thick that yield an average of 10–12 gallons per ton and contain the major part of the resources.

The hypothetical resources in the unexplored or little-sampled parts of this very widespread unit are estimated to total about 800 billion barrels of oil (Duncan and Swanson, 1965, p. 14).

OTHER SHALE DEPOSITS

In Alaska, oil shales are contained in rocks of mostly marine origin which underlie large areas in the north. These sequences range in age from Mississippian through Early Cretaceous, and consist dominantly of black shale, chert, and black organic limestone, except for the Cretaceous rocks which are dominantly sandstone and conglomerate (Donnell, Tailleur, and Tourtelot, 1967; Duncan and Swanson, 1965, p. 14). Most of the area is complexly faulted and folded, and good exposures are rare in the tundra-covered slopes. Near the Nation River in eastern Alaska, outcropping Upper Triassic oil shale that is locally 200 feet thick is reported to yield about 30 gallons of oil per ton. On the north slope of the Brooks Range, exposures of Upper Triassic through Lower Cretaceous shale contain thin zones, less than 5 feet thick, of oil shale that yields as much as 160 gallons of oil per ton. Other zones, 20 feet or more thick, are known to yield an average of 15 gallons of oil per ton. These shales also contain unusually high concentrations of trace elements such as silver, gold, and merucry. Because of the lack of data, identified resources of oil shale are extremely small, but Duncan and Swanson (1965, p. 14) estimated that hypothetical resources total about 450 billion barrels of oil, of which about 250 billion barrels would be in high-grade oil shale.

Beds of oil shale associated with coal are numerous in the United States, but they are generally thin and lean, or of small extent. Identified resources—those in carefully appraised deposits—are small. Hypothetical resources may be large.

FOREIGN OIL-SHALE DEPOSITS

Oil-shale deposits of Cambrian to Cenozoic age are abundant throughout the world in all types of depositional environments. The identified resources of shale oil in areas outside the United States total about 1.1 trillion barrels of oil (table 96). Most of the resources are in a few large groups of marine platform shale deposits, such as the Irati Formation of Permian age in Brazil, the Cambrian and Ordovician marine shale deposits in northern Europe and northern Asia, and the Jurassic deposits of western Europe and the Russian Platform, and in one large lacustrine deposit, the Triassic oil shales of central Africa (Duncan and Swanson, 1965; Duncan, 1967). Hypothetical resources total about 7.3 trillion barrels of oil, principally in the Irati Formation of Brazil, and in the Cambrian marine shale of northern Asia.

Reviews of world occurrences are summarized by Duncan and Swanson (1965), Duncan (1967), and Smith, Smith, and Kommes (1959); deposits in the U.S.S.R. are described by Kotlukov (1968), and those in Brazil by Padula (1969).

TABLE 96.—*Shale-oil resources of the world (excluding the United States) in billions of barrels, by grade (oil yield) of oil shale*

[All numbers are rounded; Ne, not estimated; from Duncan and Swanson 1965, table 3]

Continents	Identified [1]		Hypothetical [2]		Speculative [3]	
	25–100 gal per ton	10–25 gal per ton	25–100 gal per ton	10–25 gal per ton	25–100 gal per ton	10–25 gal per ton
Africa	100	Small	Ne	Ne	4,000	80,000
Asia	90	14	2	3,700	5,400	110,000
Australia and New Zealand	Small	1	Ne	Ne	1,000	20,000
Europe	70	6	100	200	1,200	26,000
North America (excluding United States)	Small	Small	50	100	1,000	23,000
South America	Small	800	Ne	3,200	2,000	36,000
Total	260	820	150	7,200	14,600	295,000

[1] Identified resources: Specific, identified mineral deposits that may or may not be evaluated as to extent and grade, and whose contained minerals may or may not be profitably recoverable with existing technology and economic conditions.

[2] Hypothetical resources: Undiscovered mineral deposits, whether of recoverable or subeconomic grade, that are geologically predictable as existing in known districts.

[3] Speculative resources: Undiscovered mineral deposits, whether of recoverable or subeconomic grade, that may exist in unknown districts or in unrecognized or unconventional form.

SPECULATIVE RESOURCES

Speculative resources of shale oil in undiscovered deposits of shale were calculated by Duncan and Swanson (1965, p. 7) as follows:

The United States is calculated to contain about 2.4 million cubic miles of sedimentary rocks to a depth of 20,000 feet, of which 0.5 percent is assumed to be shale containing 10–65 percent organic matter and yielding 10–100 gallons of oil per ton. The total yield of oil is calculated to be about 28 trillion barrels, of which about 5 percent is assumed to be from shale yielding 25–100 gallons of oil per ton. From these figures are subtracted the identified and hypothetical resources to obtain the speculative resources. Similar calculations were made to obtain the speculative resource figures shown in table 96.

Marine black shales are the primary source of the speculative shale-oil resources because they occur in large volumes in sedimentary basins all over the United States. Ordovician shales in New York, Illinois, Iowa, and Nevada are known to contain units that yield 10–25 gallons of oil per ton (Duncan and Swanson, 1965, p. 15). Permian deposits of black shale at some places contain 10–20 percent organic matter, but most samples yield little oil. In southwestern Montana, a Permian black shale may yield 10–15 gallons of oil per ton in a 600-square-mile area. In California, Miocene marine shales underlie an area of 3,000 square miles and samples show a range in yield from 3–30 gallons of oil per ton.

Carbonaceous shales associated with coal beds constitute a potentially large resource of shale oil because they occur throughout much of the United States. Duncan and Swanson (1965, table 2) estimated that these shales may yield 310 billion barrels of oil, of which 60 billion barrels would be from higher grade oil shale (25–100 gallons of oil per ton).

Lacustrine deposits seem to be the best prospect for finding new shale-oil resources in high-yield oil shale because the best deposits currently known are in the lacustrine Green River Formation of Eocene age. It is unlikely that any other deposit of the magnitude of the Green River Formation exists in the United States, because it required a unique set of conditions persisting for millions of years in extremely large shallow lakes. However, small high-grade deposits may be present in the numerous unexplored lacustrine deposits of Tertiary age in the Western United States (Feth, 1963), particularly in Montana, Nevada, and Wyoming (Duncan and Swanson, 1965, p. 16).

PROSPECTING TECHNIQUES

Oil shales can usually be recognized on the outcrop by their texture, color, and low specific gravity, but the evaluation of an oil-shale deposit requires core drilling to obtain unweathered samples that are representative of the buried deposit. Other techniques are available for use in a preliminary evaluation of a possible oil-shale deposit. If wells have been drilled through the deposit for other purposes, such as petroleum exploration, the cuttings of these wells can indicate the presence or absence of good oil shale. Geophysical logs of wells, such as sonic or density logs, can be used in some places in predicting the probable oil yield of the shales in the sedimentary sequence (Bardsley and Algermissen, 1963). For many years the U.S. Bureau of Mines has attempted to evaluate the oil-shale resources of the Green River Formation in Colorado, Utah, and Wyoming by collecting and assaying cuttings of wells. They were generally successful in indicating the boundaries of the oil-shale deposit and the approximate magnitude of the resources, but they found that individual sample sets could not be relied upon because of the possibility of contamination, or accidental enrichment, of the cuttings.

In lacustrine deposits the richest oil shale is deposited in the center of the lakes, so a geologic evaluation of the outcropping rocks in a basin may point the way to the location of the depositional center of the deposit, and thus narrow the area of intensive search.

PROBLEMS FOR RESEARCH

Oil shale in the green River Formation contains a wide variety of unusual minerals but the amount and number are imperfectly known. Much exploration and research is needed to identify the minerals, to calculate the amount and extent of potentially valuable minerals, and to investigate the feasibility of recovering them as coproducts or byproducts in a commercial oil-shale mining and retorting operation.

Research is also needed in solving the technological problems of extracting the oil at low cost and at minimum damage to the environment. Environmental problems associated with the extraction of shale oil by conventional retorting are magnified because of the large volume of rock that would be processed in a commercial operation. A plant producing 100,000 barrels of oil per day would probably mine about 130,000 tons of shale per day, and would require the disposal of a similar amount of spent shale. One problem would be to prevent the contamination of streams either by saline water encountered in mining, or by leaching of salts from spent shale. Other problems include the disposing of the spent shale and the revegetating of the spent shale if it is disposed of on the surface.

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PEAT

By Cornelia C. Cameron

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ABSTRACT OF CONCLUSIONS

Peat is no longer used as fuel in the United States. It is used for agricultural and horticultural purposes, and a demand is appearing for its use in environmental control. The physical characteristics of peat that are important to modern uses are related to the geologic and physiographic settings of the deposits; therefore, research on methods of prospecting for peat focuses on establishing geologic controls for the types of peat defined in the classification adopted by the American Society for Testing and Materials in 1969. This new classification is designed principally to characterize different types of peat by means of such physical properties as amount, kind, and size of fibers and quantity of ash. One or more types of peat occur in all but about 8 of the 50 States in magnitudes ranging from hundreds of thousands to tens of billions of tons.

The demand for specific physical qualities in peat related to modern uses and to standards for sales is largely responsible for national consumption of more peat than is produced domestically. In 1970, more than 525,000 tons of air-dried peat was produced and sold in the United States for almost $6,000,000 and 283,211 tons valued at $13,502,000 was imported, chiefly from Canada and West Germany. The forecast range of U.S. demand for peat in the year 2000 is from 1,200,000 to 2,400,000 short tons.

INTRODUCTION

Peat consists of partly decayed vegetable matter, inorganic minerals, and water in varying proportions, the usual being 10 percent solid matter to 90 percent water. Depending upon the amount of water contained, peat ranges from 0.1 to 1.6 in specific gravity and weighs 7–65 pounds per cubic foot. Hardly any two peat deposits contain material having the same physical properties. Differences are due mostly to the variety of plants from which peat is formed and to differences in climate, age of the deposit, water-level regime, and quantity of sediment deposited during accumulation of peat. Color ranges from light yellow through various shades of brown to jet black, the color representing a measure of the degree of decomposition of the peat. Peat that is newly exposed or has been well protected from the air is usually light yellow or brown. Well-decomposed humified peat is jet black. On drying in the air, most peat becomes lighter in color, except for very light varieties, which usually change to dark brown or black after being shredded and dried.

One of the chief substances formed by plants during their growth is cellulose which consists largely of carbon, hydrogen, and oxygen. If plant debris falls upon drained soil, it is vigorously at-

tacked by fungi and bacteria, and the carbon and hydrogen of the cellulose unite with atmospheric oxygen and with each other to form carbon dioxide, water, and marsh gas. If oxidation is unhampered, the organic material will disappear in a relatively short time. If, however, the plant falls into water or upon water-saturated soil where atmospheric oxygen is largely excluded, decay is slow, and if the plant debris becomes buried, a large proportion of the fixed oxygen is retained, and peat is formed. By this means, peat, which essentially has the composition $C_{62}H_{72}O_{24}$, forms from cellulose ($C_{72}H_{120}O_{60}$) by the elimination of hydrogen and oxygen as water (H_2O), carbon and oxygen as carbon dioxide (CO_2), and carbon and hydrogen as methane (CH_4) (Soper and Osbon, 1922, p. 6–7).

Peat is formed in swamps, bogs, or marshes under conditions favorable to the profuse growth of plants and to the accumulation of plant debris without complete decomposition by bacterial and chemical action. Climate, topography, and changes in position of the water table are the chief factors governing the formation and preservation of peat deposits.

The quality of peat is determined by several factors. The rate and type of water inflow and drainage control the amount of inorganic material such as silt, sand, and gravel. Fluctuation of the water table permits air to come in contact with wet peat and causes rapid decomposition, leading to partial or complete destruction of plant fibers. Such fluctuation is greatest near streams and drainage ditches. If surface conditions are unchanged, carbonization is largely arrested, and peat forms; it may continue to exist indefinitely as peat unless the land is drained and decomposition begins, or unless it is deeply buried beneath sediments and subjected to pressure and heat to form coal.

CLASSIFICATION

For statistical purposes the U.S. Bureau of Mines has classified peat into three general types—moss peat, reed-sedge peat, and peat humus. Peat of sphagnum, hypnum, and other moss types is classified as moss peat, whereas peat of reed-sedge, shrub, and tree groups is classified as reed-sedge peat. Any peat so decomposed that the botanical identity is lost is classified as peat humus. This classification, however, does not adequately identify peat according to properties demanded by modern industry, properties which are based on the use of peat as a soil conditioner and horticultural material.

Chief among these desirable properties is water-holding capacity, or the ability to reabsorb water after initial drying, like a sponge. Water-holding capacity, which is measured in percentage by weight, depends upon botanical character, the degree of decomposition, and the extent to which peat has dried. Ash content, also measured in percentage by weight, consists of the solids remaining after a test portion of dry peat has been heated at 550°C. Ash content is therefore the reciprocal of organic content valuable to peat use. Fiber content refers to the proportion of stem, leaf, or other plant fragments between the sizes of 0.15 and 12.7 mm.

To meet the need for a classification designed principally to characterize different types of peat on the basis of these and other useful properties, such as acidity and moisture content, a new classification was proposed by the American Society for Testing and Materials Committee D–29 Subcommittee I (Farnham, 1968); this classification was adopted in the form of ASTM Designation D2607–69 (Am. Soc. Testing and Materials, 1969). According to this standard, "the term peat refers only to organic matter of geological origin, excluding coal, formed from dead plant remains in water and in the absence of air. It occurs in a bog, swampland, or marsh, and has an ash content not exceeding 25 percent by dry weight." The classification lists five major plant types according to genesis and fiber content. Percentages of fiber are based on oven-dried weight at 105°C., not on volume. The five types are: (1) **Sphagnum moss peat**, in which the oven-dried peat contains a minimum of 66⅔ percent recognizable **Sphagnum** moss fiber; (2) **Hypnum moss peat**, in which the oven-dried peat contains a minimum of 33⅓ percent fiber, of which at least half is **Hypnum** moss fibers; (3) **Reed-sedge peat**, in which oven-dried peat contains a minimum of 33⅓ percent fiber, of which at least half is reed-sedge and other non-moss fibers; (4) **Peat humus**, in which oven-dried peat contains less than 33⅓ percent fiber; and (5) **Other peat**, which includes all other forms of peat not classified in ASTM Designation D2607–69.

As part of the research leading to the formulation of this new classification, analyses were made of 191 representative samples of peat sold in the United States (Farnham, 1968, p. 89). Sphagnum moss peat samples had the highest fiber contents and generally the lowest ash content and pH. Also, except for a few artificially dried materials, the water-holding capacities were well over 1,000 percent. The hypnum moss peat samples were much less acid but had slightly higher ash contents. Reed-sedge peat samples differed in pH and ash contents and had medium fiber contents and water-holding capacities. Peat humus samples were very low in fiber

content and water-holding capacity, a condition which is indicative of a high degree of decomposition.

THE WORLD PEAT INDUSTRY

Peat bogs are estimated to make up about 375 million acres of the world's land surface (Tibbetts, 1968, p. 8). Almost 80 percent of this peatland is within the boundaries of the U.S.S.R., Finland, and Canada, more than 60 percent being in the U.S.S.R. alone. According to information available in 1963, the rest of the world's resources are largely in the United States, East and West Germany, Great Britain and Ireland, Sweden, Poland, Indonesia, Norway, Cuba, Japan, Denmark, Italy, and France (table 97).

TABLE 97.—*Location of the world's peat resources, 1963*

[Source: Tibbetts, 1968]

	Percentage of world resources
U.S.S.R.	60.8
Finland	9.5
Canada	9.1
U.S.A.	5.0
Germany (East & West)	3.5
Great Britain and Ireland	3.5
Sweden	3.4
Poland	2.3
Indonesia	0.9
Norway	.7
Cuba	.3
Japan	.2
Denmark	.08
Italy	.08
France	.08
Other countries	.56

On the basis of available information, the U.S.S.R. accounts for 95 percent of the world's peat production, which was estimated in 1970 to be more than 217 million short tons per year, an increase of 7 percent over the estimated world output for 1969 (Sheridan, 1971b). Production by countries in that year is listed in table 98. Although fourth in world production after the U.S.S.R., Ireland, and West Germany, the United States produced only 0.2 percent of the world total in that year.

Only about 32 percent of the world's peat production is used for fuel, much of this being used for the generation of electric power, chiefly in the U.S.S.R. and Ireland. The generating capacity of present peat-fired power plants in Ireland is 387.5 megawatts. Some peat is used in West Germany and Finland for fuel, but this use is declining.

Most of the remaining 68 percent of the world's peat production is used for agricultural purposes; various grades of peat are produced for the amelioration of mineral soils. Other uses of peat include horticultural applications, as in the United States, Canada, and most countries of Europe; the manufacture of thermal insulating materials and chemicals in the U.S.S.R.; the making of peat planting pots in Norway, Denmark, Ireland, Czechoslovakia, Poland, and Japan; the production of activated carbon in the Netherlands; the distilling of whisky in Scotland; and uses in health spas, curative water, cosmetics, and tonics in Austria.

TABLE 98.—*World peat production in 1970*

[Source: Sheridan, 1971b]

	Thousand short tons
U.S.S.R.	206,462
Ireland	7,566
West Germany	1,467
United States	517
Netherlands	440
Canada	317
Finland	255
Sweden	138
France	80
Japan	80
Hungary	72
Israel	22
Poland	22
Norway	17
Korea	10
Denmark	6
Total	217,471

THE U.S. PEAT INDUSTRY

The use of peat in the United States for agricultural purposes began about 1904, when 12 companies produced a few thousand tons of peat annually. By 1971, peat was being extracted at 122 operations, where 120 companies produced 516,825 short tons (Sheridan, 1971a). In 1971, peat was produced in 24 States (see fig. 62), but 8 States bordering the Great Lakes had more than half the active pits. Michigan, with 20 had the largest number of operations, followed by Colorado, with 15; Ohio and Pennsylvania, with 11 each; Washington, with 9; and Florida and Minnesota, with 8 each. Thirty-seven plants produced moss peat, 39 plants produced reed-sedge peat, and 33 plants produced humus. In addition to plants producing these types of peat, 13 plants produced two or all three types. Peat produced in the United States in 1970, by types, is shown in table 99.

Commercial sales of peat for 1970 totaled 525,603 short tons valued at $5,986,000, averaging $11.39 per ton (Sheridan, 1971a). Table 99 shows production of peat by types, and table 100 shows production and sales of peat by States in 1970. In addition, 283,211 short tons valued at $13,502,000 were imported, chiefly from Canada and West Germany, as shown in table 101.

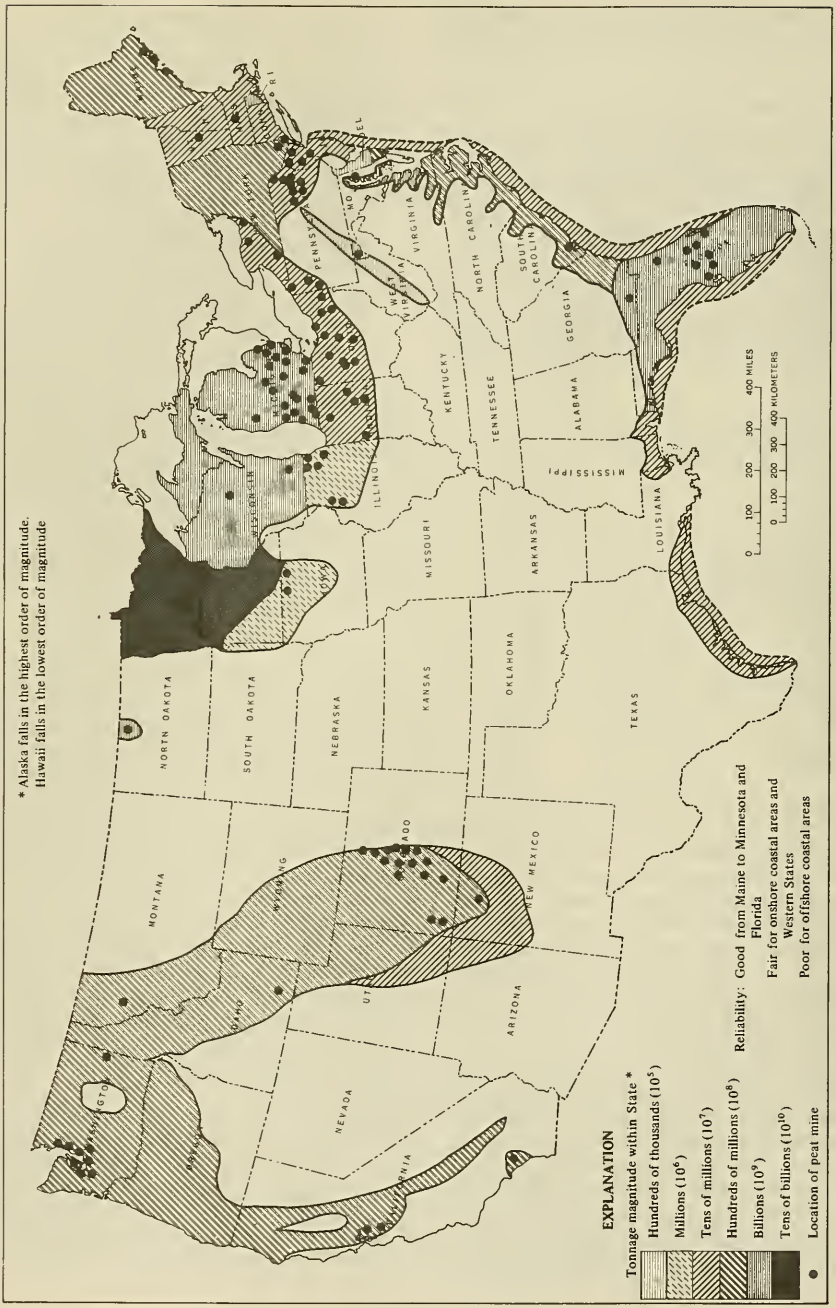

FIGURE 62.—Peat mines in operation in 1971 and estimated resources in short tons of air-dried peat suitable for commercial use.

TABLE 99.—*Peat produced in the United States in 1970, by type*

[In short tons. Source: U.S. Bur. Mines; Sheridan, 1971b]

Type	Unprepared	Processed			Total
		Shredded only	Kiln-dried only	Shredded and kiln-dried	
Moss	48,718	79,161	----	2,135	130,014
Reed-sedge	26,486	223,374	750	----	250,610
Humus	41,925	90,633	3,643	----	136,201
Total	117,129	393,168	4,393	2,135	516,825

TABLE 100.—*Production and commercial sales of peat in the United States, by States, 1970*

[W, withheld to avoid disclosing individual company confidential data; included in total. Source: U.S. Bur. Mines; Sheridan, 1971b]

State	Active plants	Production (short tons)	Commercial sales		
			Short tons	Value	
				Total (thousands)	Average per ton
California	3	9,792	9,792	W	W
Colorado	[1] 15	34,240	34,499	$210	$6.08
Florida	8	45,743	45,742	304	6.65
Georgia	1	432	432	W	W
Idaho	1	W	W	W	W
Illinois	6	W	W	W	W
Indiana	5	W	W	W	W
Iowa	2	W	W	W	W
Maine	[2] 3	1,223	1,000	39	39.00
Maryland	2	4,588	3,633	47	12.94
Massachusetts	1	2,000	2,000	30	15.00
Michigan	[1] 20	156,699	166,950	1,896	11.36
Minnesota	8	13,948	13,377	335	25.04
Montana	1	W	W	W	W
New Jersey	4	45,260	45,260	557	12.30
New Mexico	1	500	500	7	13.00
New York	5	15,325	14,525	145	9.98
North Dakota	1	W	W	W	W
Ohio	11	6,357	6,357	95	14.94
Pennsylvania	11	49,284	43,793	517	11.81
South Carolina	1	W	W	W	W
Vermont	1	338	244	6	24.59
Washington	9	16,625	16,625	71	4.27
Wisconsin	2	1,581	1,650	W	W
Total	122	516,825	525,603	5,986	11.39

[1] Excludes one plant which had sales, but no production.
[2] Includes one plant which had production, but no sales.

TABLE 101.—*Peat moss imported for consumption in the United States, by grade and by country, 1970*

[Source: U.S. Bur. Mines; Sheridan, 1971b]

Country	Poultry and stable grade		Fertilizer grade		Total	
	Short tons	Value (thousands)	Short tons	Value (thousands)	Short tons	Value (thousands)
Belgium-Luxembourg	------	------	22	[1]	22	[1]
Canada	1,679	$94	267,944	$12,792	269,623	$12,886
Finland	7	[1]	------	------	7	[1]
Germany, West	86	3	9,919	429	10,005	432
Ireland	4	3	960	46	964	49
Japan	------	------	30	2	30	2
Mexico	------	------	24	1	24	1
Norway	6	4	7	4	13	8
Poland	------	------	1,950	88	1,950	88
Spain	------	------	7	5	7	5
Sweden	------	------	449	22	449	22
United Kingdom	------	------	117	9	117	9
Total	1,782	104	281,429	13,398	283,211	13,502

[1] Less than ½ unit.

All humus and reed-sedge and some moss peat production is from surface pits, and most operations use conventional types of excavating and earth-moving machinery, including bulldozers, draglines, and front-end loaders in drained bogs, and clamshells and dredges for submerged deposits. Use of specialized machines for cutting sphagnum moss is replacing the ancient practice of hand cutting sphagnum moss blocks, especially in large bogs in Maine. Peat is prepared for sale by shredding and screening; some is dried artificially.

Before 1955, most domestic peat was sold locally in bulk, but since then, large quantities have been packaged and distributed to all parts of the United States. Prices of domestic peat vary greatly; in general, the sales value depends chiefly on the type of peat, the degree of processing, and whether the peat is sold in bulk or packages. In 1970, the average value of bulk peat was $8.13 per ton, $0.46 more than the average value of bulk peat sold in 1969. Packaged peat, however, declined in average value from $17.60 per ton in 1969 to $14.51 per ton in 1970. Commercial sales of peat in the United States in 1970 are shown in table 102.

TABLE 102.—*Commercial sales of peat produced in the United States in 1970, by use*

[Source: U.S. Bur. Mines; Sheridan, 1971b]

Use	In bulk		In packages		Total [1]	
	Quantity (Short tons, thousands)	Value (thousands)	Quantity (Short tons, thousands)	Value (thousands)	Quantity (Short tons, thousands)	Value (thousands)
Soil improvement	193	$1,616	257	$3,421	450	$5,038
Potting soils	14	118	6	221	20	338
Packing flowers, shrubs, etc.	40	298	2	37	42	336
Seed inoculant	---	-----	3	206	2	206
Mushroom beds	3	29	(1)	(1)	3	29
Earthworm culture	1	9	(1)	2	1	11
Mixed fertilizers	6	27	---	-----	6	27
Total [2]	258	2,098	268	3,888	526	5,986

[1] Less than ½ unit.
[2] Data may not add to totals shown because of independent rounding.

Although the average value of imported peat is more than three times that of domestically produced packaged peat, the two are not comparable because they are assigned at different marketing levels. Also, imported peat has different physical properties and is usually sold by volume rather than by weight. Each 100 pounds of typical air-dried imported peat measures approximately 12 bushels, whereas the same quantity of a typical domestic peat measures 3 or 4 bushels. Only a few U.S. peat operators produce peat with properties similar to those of the imported type.

The quantity of peat imported into the United States in 1970 decreased 6 percent from that imported in 1969, mainly because of decreased shipments from Canada. European shipments to the United States decreased 9 percent, mainly because of the smaller quantities shipped from Ireland and Poland. Shipments from West Germany supplied almost three-fourths of the peat imported from Europe.

PEAT DEPOSITS

Soper and Osbon (1922) recognized three general types of peat deposits, according to topography. These include the filled basin, in which peat accumulates in marshes, ponds, and lakes; the built-up deposit and its corollary, the climbing bog, in which peat forms on flat or gently sloping moist areas not covered with water; and the composite area consisting of built-up peat underlain by peat of the filled-basin type.

The filled-basin type is predominant. Beginning at the center of basins filled with water and proceeding shoreward, the usual sequence of vegetation is algae, pondweeds, water lilies, bullrushes, and amphibious sedges. Sphagnum and heath shrubs sometimes grow on the marginal zones and are abundant on the quaking bogs of the Northern States. Adjoining zones of vegetation usually overlap, and some zones may be absent. Unless the water is shallow enough to permit plants to take root, fine-grained algal peat is normally at the bottom of filled-basin deposits and is overlain by strata of reed, sedge, and grass peat. Fire, drought, and drainage, however, may prevent formation of successive growth and decay of plant associations, and changes in the surface water from alkaline to acid may also affect composition of flora.

Salt-marsh peat fills basins in much the same manner as fresh-water peat but differs from it somewhat in character. Because few seed plants tolerate salt water, the number of plant varieties in salt marshes is small. Salt-marsh peat is composed

of salt-marsh grasses, rushes, and sedges. In some of the coastal marshes, salt-marsh peat is underlain by peat of fresh-water origin, indicating subsidence of part of the coast.

Built-up deposits consist of moss and heath, overlain by tamarack-spruce in the north and by gum-cypress in parts of the Atlantic and Gulf coastal regions. The ground water level, although it may never rise above the surface, is progressively elevated as the peat collects. Surface conditions are little changed from year to year; hence, built-up bogs are relatively homogeneous.

When a basin is filled with peat to the level of the surrounding country, it is mature, and if moisture is sufficient, the build-up process begins; the deposit develops as if it had originated on a relatively level land surface not covered with peat. The result is a composite peat deposit which may accumulate to a thickness of many feet above the former level of the basin. Composite areas are recognized by marked changes in the character of the peat where the pondweeds, water lilies, and sedges were displaced by moss and heath plants.

As the formation of peat depends upon many factors, the rate of its accumulation varies widely from place to place and from year to year. If climate, topography, and vegetation are favorable, peat forms rapidly, as in a few sphagnum bogs along the coasts of Maine and Alaska, but if one of these factors becomes relatively unfavorable, the rate of accumulation is retarded or brought to a stop, or destruction of the deposit may set in. Most if not all peat deposits that formed during the Pleistocene were erased by weathering or erosion, so that the present deposits, all of Holocene age, may lie on truncated remnants of older cycles of peat development. An age of about 13,000–14,000 years is about the maximum for a commercial peat deposit. Unlike timber stands, most peat deposits in the United States are not renewable.

The major peat deposits in the conterminous United States occur (1) north of the 41st parallel and east of the 97th meridian in all the New England States, Illinois, Indiana, Iowa, Michigan, Minnesota, New Jersey, New York, Ohio, Pennsylvania, and Wisconsin; (2) in the Atlantic and Gulf coastal regions; and (3) in the western mountains and coastal areas including parts of Washington, Idaho, Montana, Oregon, California, Wyoming, Utah, Colorado, Arizona, and New Mexico.

In the northeastern and north-central region, peat has accumulated chiefly in former lakes and ponds in glacial terrain. Built-up deposits of sphagnum moss peat are largely restricted to the cool humid northern parts of the Midwest and New England.

The Atlantic and Gulf coastal regions are characterized by many salt- and fresh-water marshes and swamps; the peat deposits occur principally in valleys and lagoons on a gradually subsiding coastal plain. This peat is made up mostly of salt-marsh grasses and other salt-water plants. However, many deposits also have an underlayer of peat formed from fresh-water plants. This layer was deposited before the basin was invaded by salt water.

Peat deposits of the West (Jennings, 1966, p. 288; Cameron, 1968; Huntting, 1966; Savage, 1964) are in basins in glaciated mountains and plains, in tidal plains, and in river plains.

The cool moist climate and irregular terrain of Alaska favor the formation of all types of deposits, but especially the built-up sphagnum moss type. Small pockets of peat occur in high volcanic uplands in Hawaii.

GEOLOGIC AND PHYSIOGRAPHIC FACTORS THAT CONTROL QUALITY AND QUANTITY

The minimum size of a peat deposit worth exploiting in the United States differs from place to place. In the glaciated areas of the North, West and Northwest, and in broad coastal marshes elsewhere, peat deposits now exploited are at least 10 acres in areal extent and have at least a 5-foot thickness of commercial-quality peat. Tonnage in peat deposits is calculated on the basis of 200 tons of air-dried peat per acre-foot.

On the basis of these criteria, high-quality sphagnum moss peat may be expected in large raised bogs in New England, especially in Maine, and in northern Minnesota. Most of the peat in the United States, however, is reed-sedge, humus, and other types deposited largely in basins. The quality and quantity of these deposits are dependent upon constant factors such as size, shape, and composition of the depression containing the deposit, and upon varying factors such as climate and surface- and ground-water drainage. Cameron (1970a, b, c), working in the glaciated areas of Pennsylvania and New York and the unglaciated uplands of West Virginia, Maryland, and Pennsylvania, listed relationships of these factors significant to resource potential of peat deposits as follows:

1. Peat deposits enclosed within a bedrock basin tend to have a higher percentage of fibers longer than 0.15 mm than those deposits surrounded by unconsolidated material. Relationship of peat quality to kind of material composing the surrounding area and the walls of the depression in which accumulation of peat took place involves several aspects,

such as water-transmitting characteristics, solubility, resistance to erosion, and degree of weathering of the material next to the peat.

2. Within unconsolidated material, peat deposits larger than several acres in areal extent tend to have lower ash content and a higher percentage of fibers longer than 0.15 mm than do similar smaller deposits.

3. Peat deposits in depressions with high steep walls tend to be thicker than deposits in depressions with low gently sloping walls. Steep walls favor rapid build-up of marsh-type vegetation above the original pond-surface level and at the same time delay development, along the margins of the depression, of soil conditions that initiate transgression of a forest, which slows and eventually stops peat formation.

4. Peat deposits accumulated in depressions with high steep stable walls are apt to have lower ash content than deposits in depressions with unstable walls.

5. Peat deposits in depressions having small drainage basins tend to contain less clay, sand, and silt than do deposits in depressions having larger drainage basins. The ratio of effective drainage area to area of peat accumulation in more than 100 deposits in northeastern Pennsylvania showed that if the sediment-producing area is more than 10 times the size of the area of peat accumulation, the ash content of the peat is apt to be greater than 25 percent.

6. Peat deposits accumulating in a cool, moist climate are thicker and have lower ash content than deposits accumulating in a cool, dry climate. Humidity is the controlling factor in growth of peat-producing plants and preservation of plant structures.

7. Peat deposits protected topographically from stream flooding are apt to have lower ash content than deposits subject to flooding. Two common causes of flooding are increased precipitation and ponding resulting from landslides or beaver activity.

8. Peat deposits subject to water-table fluctuation caused by (a) artificial drainage, (b) drainage caused by breaching of dams on adjacent streams, or (c) lumbering operations and extensive forest fires, which extinguish springs and seeps, have higher ash content and a lower percentage of fibers longer than 0.15 mm than do deposits not subject to water-table fluctuation. This is because a deposit saturated with ground water is relatively free from aerobic bacterial activity which decays vegetable matter. When the water table falls, permitting oxygen to enter the deposit, decay increases ash content by destroying plant fibers.

RESOURCE POTENTIAL AND OUTLOOK

The latest nationwide study of the occurrence and use of peat was by Soper and Osbon in 1922; emphasis was on potential use as fuel, and deposits were not appraised with the restrictive criteria of present use. Moreover, since 1922, many peat deposits have been destroyed, and many new areas probably containing much peat have been made accessible by modern roads. Therefore, the 14 billion tons estimated by Soper and Osbon is no longer realistic for peat that meets the ash and fiber-size specifications of modern uses. Measurement of such resources in unexploited deposits is only just beginning. The data on figure 62 and table 103, although based on very scanty quantitative information and little known geologic and physiographic controls, are an attempt to approximate the magnitude of potential resources for each State.

TABLE 103.—*Approximate magnitude of potential resources*[1] *of peat estimated for each State*

[Distribution shown on fig. 62]

State	Short tons of air-dried peat
Delaware, Hawaii, Maryland, North Dakota, West Virginia	10^5
Illinois, Iowa, Rhode Island, South Dakota	10^6
Alabama, Arizona, Connecticut, Indiana, Louisiana, Massachusetts, Mississippi, New Hampshire, New Jersey, New Mexico, Ohio, Pennsylvania, Texas, Vermont	10^7
California, Colorado, Georgia, Idaho, Maine, Montana, New York, North Carolina, Oregon, South Carolina, Utah, Virginia, Washington, Wyoming	10^8
Florida, Michigan, Wisconsin	10^9
Alaska, Minnesota	10^{10}

[1] Potential resources: Identified mineral deposits not profitably recoverable with existing technology and economic conditions, and undiscovered mineral deposits whether of recoverable or subeconomic grade.

Refinements in prospecting for deposits in these States will result from close coordination of physical-property requirements, given in the recent ASTM peat classification, with the geologic and physiographic factors that control quality and quantity. Although the present physical-property requirements are largely for agricultural uses, they are much the same as those for the growing use of peat in environmental control. For example, D'Hennezel and Coupal (1972) have shown that moss peat, because of its very high water-holding capacity, can be used on a large scale in combating pollution caused by oil spills from offshore drilling and from freighters and barges.

Extensive research by the Department of Chemical Engineering of the University of Sherbrooke, Quebec, Canada, has revealed the high efficiency of

moss peat in the filtration of pigments and dyes in wastes from textile plants, and of mercury and other metals in wastes from other industrial plants; moss peat is 20 to 30 times cheaper than activated charcoal presently used as a filtering agent.

Moss peat can now be used for the manufacture of activated carbon, as a binder for pelletizing iron-ore concentrates, and for manufacture of concretes used as lightweight thermal and sound insulators.

Decarlo (1970) forecasted that the national demand for peat for the year 2000 will reach 1,200,000 to 2,400,000 short tons.

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PHOSPHATE DEPOSITS

By James B. Cathcart and R. A. Gulbrandsen

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ABSTRACT OF CONCLUSIONS

Phosphorus, an element essential to plant growth, is found in igneous apatite, guano or related deposits, and marine phosphorite. Most of the United States' and the world's reserves and resources are in the marine phosphorite deposits which also account for about 75 percent of the total production.

Marine phosphorite deposits, known throughout the world in rocks ranging in age from Precambrian to Holocene, form in basins away from sources of abundant clastic material in warm latitudes in areas of upwelling water.

Because most of the sedimentary basins are known and phosphate occurs in many of them, resources are classed as identified or as hypothetical. Speculative resources form only a minor part of the total. However, identified resources of the world are measured in billions of tons of contained phosphorus and hypothetical resources are probably many times as great.

A major factor of concern is the transportation of a bulk, low-value product to areas of use. Many problems, however, remain to be solved, particularly in the accurate delineation of reserves in the large areas of probable hypothetical resources and in the mining and beneficiation of deeply buried and low-grade resources.

Environmental problems attendant upon open-pit mining and chemical processing must be solved. Failure to solve these problems in the United States may lead to drastic changes in the traditional supply patterns of phosphate rock in the world.

Phosphate rock contains abundant fluorine and potentially economically recoverable amounts of vanadium, uranium, and the rare earths. Trace metals necessary to plant growth, such as boron, copper, molybdenum, manganese, and zinc are present in phosphate rock, are removed during chemical processing, and are readded to make a complete fertilizer. Chemical research on problems of recovery of minor elements and the retention in chemical fertilizer of the trace metals is needed.

INTRODUCTION

Phosphorus is one of the three elements vital to plant growth, but it tends to be less abundant than the other two (nitrogen and potassium), particularly in soils that have been extensively cropped or in tropical soils that are thoroughly leached by acid ground water.

About 70 percent of the domestic consumption of phosphate rock is in fertilizers, and the major use will continue to be in fertilizers because there is no substitute for phosphorus as a plant food element. Other uses are many; they include animal feed supplement, detergent, electroplating and polishing of metals, insecticides, medicines, and incendiary bombs.

Phosphate fertilizers are used extensively in the developed countries, but are used sparingly or not at all in some of the less developed countries. Production of agricultural materials is limited by deficiency in plant nutrients, and chemical fertilizers, including phosphorus, are vital to the production of adequate food in the world.

Phosphorus is found in minable concentrations in three principal environments—guano or deposits derived from guano, igneous apatites, and marine phosphate deposits. Other types of concentrations such as phosphatized rock, residual phosphate, and river pebble deposits are secondarily derived.

All types of deposits are found in the United States and are widely distributed areally and geologically. Occurrences of phosphate rock are known from almost all geologic eras from Precambrian to Cenozoic, and in almost all of the States, but in 1971, phosphate rock was produced only from Ordovician rocks in Tennessee and Alabama; from Permian rocks in Idaho, Montana, Utah, and Wyoming; and from Miocene and Pliocene rocks in Florida and North Carolina. Some production from the Miocene of California is included in the totals for the Western States. Production in 1971 was about 38 million short tons, of which 83 percent was from Florida and North Carolina, 11 percent from the Western States, and 6 percent from Tennessee. About 27 million tons was used domestically; the rest was exported.

Reserves of phosphate rock in Florida, North Carolina, and the Western States are measured in billions of tons in each area; Tennessee reserves are in millions of tons. These reserves can supply domestic demands for scores or hundreds of years, but political, economic, and ecological demands may radically alter the traditional supply patterns in the United States, and at some time in the future the supply of phosphate rock to the eastern seaboard may possibly come from foreign sources.

World production of phosphate rock in 1970 was about 94 million tons. About 75 percent of the production came from marine phosphorite, 17 percent from igneous apatite, and the rest from guano-derived deposits. The United States produced about 40 percent, the U.S.S.R. about 20 percent, and North Africa about 20 percent.

Reserves of phosphate rock in the world are measured in scores of billions of tons and resources are equally vast. Most of the reserves and resources are in the marine phosphorites; reserves in igneous apatite are large but account for only a small percentage of the total and those in guano or guano-derived deposits are limited.

EXPLOITATION

The first record of phosphate rock mining was in 1847 when a few tons of nodules ("coprolites") were produced from Pliocene beds near Suffolk in England; mining of igneous apatite began in 1851 in Norway. Mining of rock phosphate began after the discovery of Leibig and Lawes that bones and phosphate rock treated with sulfuric acid increased crop response.

The first mining of rock phosphate in North America was of pegmatite apatite in Canada that started in about 1863; mining in the United States began in 1867, when a few tons of South Carolina phosphate rock was produced. By 1870, production in the United States had reached 65,000 tons (table 104). Production of phosphate from Florida began in 1888, in Tennessee in 1894, and in the Western States in 1906. The maximum production of phosphate from South Carolina coincided with the start of production from Florida (table 104). The coincidence was due to the lower costs of producing from the much more extensive Florida deposits, and the increased Florida production eventually brought about the closing of the mines in South Carolina.

Tennessee production is mostly from residual "brown rock" deposits and has steadily increased from 1894 to about 1965, except for a slight decline in the depression years of the 1930's. For the past several years, the rate of increase of production from Tennessee has lessened and production in 1970 was slightly less than production in 1969.

The first production of phosphate rock in Florida was a few thousand tons in 1888. Rate of production increased rapidly and by 1920 was 3 million tons per year. The rate of production decreased during the depression and war years of the 1930's and 1940's, and then increased rapidly; as a result by 1970 the production was 31 million tons. Production has leveled off in the last few years; 1969 and 1970 showed slight decreases from the maximum year 1968, but 1971 showed a slight increase.

Production of phosphate from the Western United States began in 1906 and has increased steadily to

TABLE 104.—*Marketed production of phosphate rock in the United States in each 10th year of the period of 1870 to 1970 and total production through 1971*

[In thousands of long tons. Data from U.S. Geological Survey "Mineral Resources of the United States" and U.S. Bureau of Mines "Minerals Yearbook"]

Year	South Carolina	Florida	Tennessee	Western States	Others [1]	Total
1870	65	----------	----------	----------	------	65
1880	190	----------	----------	----------	------	190
1890	464	47	----------	----------	------	511
1900	329	706	454	----------	1	1,490
1910	180	2,068	393	10	5	2,656
1920	44	3,369	621	56	13	4,103
1930	----------	3,749	611	67	------	3,927
1940	----------	2,845	994	163	------	4,002
1950	----------	8,068	1,384	783	------	10,253
1960	----------	13,251	1,927	3,024	------	18,202
1970	----------	[2] 31,278	[3] 3,163	[4] 4,297	------	38,739
Total production through 1971	13,358	494,896	79,983	66,334	207	654,778

[1] Alabama, Arkansas, and Pennsylvania in 1900; Arkansas in 1910; Kentucky in 1920.
[2] Includes north Florida and North Carolina in 1970.
[3] Includes Alabama in 1970.
[4] Includes California in 1970.

more than 4 million tons in 1970. Production has leveled off somewhat in the last several years because of the general soft market for phosphate rock.

The total production of phosphate in the United States has almost doubled in each succeeding decade since 1870 (table 104), except for the depression and war years, and by 1970 production had reached 38 million tons.

Total production of phosphate rock in the United States is about 654 million tons through 1971—76 percent from Florida, 12 percent from Tennessee, 10 percent from the Western States, and 2 percent from South Carolina.

GEOCHEMISTRY

Phosphorus is widely distributed in the earth's crust, which contains about 0.23 percent P_2O_5. Most of the phosphorus occurs in minerals of the apatite group $Ca_{10}(PO_4,CO_3)_6(F,OH,Cl)_2$. The structure of apatite is such that small amounts of VO_4, As_2O_4, and SO_4 substitute for PO_4, and Na, Sr, U, Th, and the rare earths may substitute for Ca.

Apatite is relatively insoluble in alkaline or neutral waters, and its solubility increases as acidity increases and temperature decreases. Thus, although apatite may be residually concentrated in the first stages of weathering, it eventually breaks down. Some of the phosphate may be redeposited locally. In limestone terranes, apatite is again formed; in igneous terranes, iron and aluminum phosphates (variscite and strengite) are formed; and in clay soils, aluminum phosphates (wavellite and crandallite) are formed.

Phosphorus is carried to the sea as phosphate minerals adsorbed on iron or aluminum hydroxides or clays, in particulate or dissolved organic compounds, or in solution.

The ocean is nearly saturated with phosphate, but the phosphate content of the ocean is not uniform. Deep cold water contains about 0.3 ppm PO_4 and warm surface water contains about 0.01 ppm. In the ocean, cold, nutrient-rich waters may be brought to the surface in several ways—by divergence upwelling, dynamic upwelling, turbulence, and convection. The solubility of phosphate in upwelling waters decreases as temperature and pH increase near the surface, and apatite may then be precipitated by organic or inorganic processes. Phosphorites and the accompanying rocks in the environment of upwelling—black shale, chert, and limestone—are depositional products from sea waters that change in composition as the result of physical, chemical, and biologic processes.

TYPES OF DEPOSITS

Minable concentrations of phosphate are found in igneous rocks, as sedimentary phosphorite, and as guano, or in deposits derived from guano. The term "phosphate rock" is applied to any rock that contains more than about 20 percent P_2O_5. "Phosphorite" is equivalent, but is usually applied only to marine phosphate rocks.

IGNEOUS APATITES

Apatite occurs as intrusive masses or sheets, as hydrothermal veins or disseminated replacements, as marginal differentiations, or as pegmatites. Largest are the intrusive masses, which are commonly as-

sociated with alkaline igneous rocks including carbonatite, ijolite, nepheline syenite, and pyroxenite. The larger deposits in the world are in the Kola Peninsula (U.S.S.R.), eastern Uganda and Palabora in Africa, and Araxa and Jacupiranga in Brazil.

Reserves in individual deposits are measured in scores to hundreds of millions of tons. The phosphate mineral is a fluorapatite. P_2O_5 contents are as high as 36 percent, and weathering may form apatite-rich residual deposits overlying the surface of calcitic or dolomitic source rocks.

Other forms of igneous apatite deposits are smaller and are lower in P_2O_5 content. Examples in the United States include the ilmenite-apatite deposits of Virginia and the apatite-magnetite marginal deposits of the eastern Adirondacks. None of the deposits in the United States are being mined, and reserves and resources of this type of material are very small as compared with total resources of phosphate rock.

About 17 percent of the world's production of phosphate is from deposits of igneous apatite; most of this is from the Kola Peninsula and Palabora.

GUANO AND RELATED DEPOSITS

All large accumulations of guano are formed at the surface by sea birds. Smaller quantities are formed in caves principally by bats. Reserves in most deposits are measured in thousands or hundreds of thousands of tons. The mineralogy of guano deposits is complex inasmuch as it depends on the amount of leaching by surface waters. Slightly decomposed deposits consist of ammonium and alkali oxalates, sulfates, and nitrates, and magnesium and ammonium-magnesium phosphates. Decomposed guano consists chiefly of calcium phosphates—monetite and whitlockite.

In areas of even slight rainfall, the soluble phosphate of guano is carried downward and replaces or alters the underlying rock. Apatite is the mineral formed where the underlying rock is limestone, and, over geologic time, deposits measuring scores of millions of tons have been formed on some of the islands of the western Pacific. Aluminum or aluminum-iron phosphates (strengite and variscite) are formed where the underlying rock is volcanic. Deposits are known in several parts of the world (Malpelo Island, Colombia), but reserves are limited and processing costs are high.

Guano has been mined from caves in various parts of the United States, but reserves and resources are negligible and world resources are small. Production of guano, largely from renewable sources, measured in terms of its phosphate content, is less than 1 percent of the total production of phosphate in the world.

Guano-derived deposits, particularly those in the western Pacific account for almost 5 percent of the world's production of phosphate. Reserves are measured in millions of tons.

SEDIMENTARY PHOSPHORITE

About 75 percent of the world's production of phosphate rock is from deposits of marine phosphorite. The richest and largest of these deposits form in warm latitudes, mostly between the 40th parallels and in areas of upwelling caused by divergence. These areas are in the tradewind belts on the west coasts of the continents or in mediterranean seas along the equatorial side of the basin.

Significant concentrations also form along the west sides of poleward-moving warm currents along the eastern coasts of continents. In these areas there are cool coastal countercurrents, such as along the eastern coast of the United States.

DEPOSITS CAUSED BY DIVERGENCE UPWELLING OF SEA WATER

Deposits caused by divergence upwelling are characterized by a suite of rocks that consists, in a shoreward direction, of black shale, phosphatic shale, phosphorite, dolomite, chert or diatomite, and saline deposits and red or light-colored sandstone or shale. The rocks grade laterally into one another, and because of lateral shifts in environment due to epeirogenic movements, the sequence may also be repeated vertically. The thickest accumulations of phosphorite form in areas of geosynclinal subsidence where clastic sedimentation is at a minimum; that is, a miogeosynclinal environment. Phosphorites are also found in the eugeosynclines, but are so mixed with the thick shale, chert, and volcanic materials of the eugeosyncline that thick high-grade deposits are not known and are unlikely.

The phosphate in these rocks is carbonaceous and consists of pellets, some nodules, and minor phosphatized bone material and shell. The pellets may have formed by direct precipitation or by diagenesis, and some are certainly replaced calcite (as for example, the phosphatized shell material). Individual beds may be several feet thick and contain 30 percent or more P_2O_5, and the beds may extend over hundreds of square miles. Phosphorite that was formed on the adjacent stable continental shelf area is generally associated with chert, calcareous chert, and light-colored sandstone and shale. The phosphate consists of nodules, pellets, and abundant phosphatized shell and bone material; phosphatic sandstone

is a common textural type. Individual beds tend to be thinner than in the geosynclinal environment, but some beds thicken locally. P_2O_5 contents are generally between 20 and 30 percent.

Examples in the United States of phosphorite deposited from upwelling water caused by divergence include the Permian Phosphoria Formation of the Western United States, the Miocene Monterey Formation of California, the Mississippian and Triassic deposits of Northern Alaska, and the Mississippian deposits of Utah. The very large deposits of Kara Tau in the U.S.S.R., the Miocene deposits of the Sechura Desert in Peru, the Cretaceous of Colombia, the Cambrian of Australia, and the extensive deposits of Cretaceous and Eocene age in Western and Northern Africa and the Middle East are also of this type.

DEPOSITS FORMED IN WARM CURRENTS ALONG EASTERN COASTS

Phosphorites formed in warm currents along the eastern coasts of continents consist of phosphatic limestone or sandstone. Black shale and chert are not found with these deposits, although some diatomaceous material may be present. The deposits are generally lower in amount of phosphate per unit area than are the miogeosynclinal deposits. The most important deposits of this type are those of the Eastern United States—Florida, Georgia, and North Carolina. Phosphate in the Upper Cretaceous Gramame Formation near Recife in Brazil is another example.

Deposits of this type are economic only when they have been reworked by submarine currents, subjected to weathering, or both. Most deposits of this type must be further upgraded by some method of beneficiation after mining to provide an economic product.

The deposits along the eastern coast of the United States are of middle Miocene age and extend from southern Florida to southern Virginia. The richest deposits are found in basins of structural lows on the flanks of domes that were rising at the time of phosphate deposition. The phosphorite may have been deposited by dynamic upwelling or by the cool countercurrent associated with the warm density current. Turbulence caused by the divergence of the cool coastal current due to the rising positive area may have assisted in deposition.

Concentrations of organic growth and nutrients are found near the mouths of large rivers or in estuaries in which the outflow of surface waters is replaced by a countercurrent of sea water. Decaying organic material sinks and is trapped in the inflowing sea water. Nutrients may accumulate in the system, and the estuaries may thus have a higher phosphate content than adjacent river or sea water.

Such a process may account for the fact that the richer phosphate deposits in the Eastern United States are in the bays or basins (some of which may have been estuaries). At least this process may initiate precipitation. A combination of processes probably was operative during the formation of the phosphate deposits of the Eastern United States.

Deposits of phosphate in eugeosynclinal sediments, associated with chert, shale, and limestone, have been found in Nevada. The phosphate beds are thin and low in P_2O_5 content and are not likely to be an economic source of phosphate rock in the forseeable future.

DEPOSITS FORMED ON STABLE SHELVES OR IN CONTINENTAL INTERIORS

The marine phosphate deposits that form on the stable shelf or in the continental interior are associated with limestone, dolomite, shale, and glauconitic sandstone. The phosphate is in the form of nodules or grains that are large with respect to the matrix in which they are found. Individual beds are only a few feet thick, but commonly several beds contain phosphate. The phosphate beds contain from 5 to 15 percent P_2O_5, but the nodules may contain as much as 35 percent.

Examples of deposits of this type in the United States include beds in the Maquoketa Shale of Ordovician age in Illinois, Iowa, and Wisconsin; several formations of Ordovician age in Minnesota and Arkansas; the Oriskany Sandstone of Devonian age in New York, Pennsylvania, and Virginia; sandstone of Mississippian age in Tennessee and Arkansas; black shale of Pennsylvanian age in Kansas, Missouri, and Oklahoma; shale of Pennsylvanian age in Arkansas; several beds of Cretaceous age in Alabama, Mississippi, Georgia, and Texas, associated with limestone; and beds of Cretaceous and Paleocene age in Texas, Tennessee, Alabama, and Mississippi, and the northern Atlantic Coastal Plain, associated with glauconite.

Some of the beds have been mined—for example, Mississippian sandstone of Tennessee, called "bluerock," and the Ordovician Cason Shale and Pennsylvanian Hale Formation in Arkansas—but production was small. Reserves are small and resources are at best moderate, but these types of deposits could serve as local sources of phosphate rock in the future.

CONCENTRATION AND ENRICHMENT OF MARINE DEPOSITS

The richest of the marine deposits have been concentrated or enriched by secondary processes. For example, the deposits in the Bone Valley Formation of Florida were formed by submarine reworking of a phosphate-rich residuum. Leaching related to Pleistocene and modern weathering has further upgraded the deposits. The occurrence of phosphate gravels at unconformities is caused by weathering and reworking.

River-pebble deposits occur as bars and in the flood plains of streams that drain phosphate areas in Florida, Georgia, and South Carolina. The streams concentrate coarse-grained phosphate particles because of their size and specific gravity. Fine-grained phosphate particles, quartz sand, and clay are carried downstream, and the river-pebble deposits consist of coarse-grained phosphate nodules and quartz grains. The phosphate particles are low in P_2O_5 content because of leaching by the acid waters of the stream.

Chemical weathering of phosphatic limestone in a humid climate results in the removal of the soluble calcium carbonate and the consequent enrichment and concentration of the phosphate. The "brown rock" phosphatés of Tennessee and Kentucky are examples. Individual deposits are not large but they are grouped in such a way that the mined material can be hauled to a central recovery plant. The composition of the phosphate particles and their mineralogy are about the same as the composition and mineralogy of the marine phosphorite from which they were derived.

The apatite mineral of sedimentary rocks is taken into solution by acid ground water, and P_2O_5 may be precipitated if the solutions pass through aluminum- or iron-bearing rocks or through limestone. Secondary deposits in limestone areas, such as the white rock of Tennessee and the hardrock of Florida, consist of phosphate incrustations or irregular replacement. The P_2O_5 content depends on the degree of replacement; some replacement deposits are very high in phosphate content. Deposits are irregular in shape and are generally small.

OTHER TYPES OF PHOSPHATE DEPOSITS

Other sources of phosphate include bone piles, glauconite, and phosphatic iron ores that yield a basic slag in the Bessemer or basic open-hearth manufacture of steel. Bone piles are no longer an important source of phosphate. Glauconite (green sand) contains both K_2O and P_2O_5 and has some use as a fertilizer; reserves and resources in the Cretaceous and Paleocene of the Atlantic Coastal Plain are very large. Phosphatic iron ore includes marine deposits like the Red Mountain Formation of Alabama as well as apatite-magnetite deposits. Basic slag (Thomas Meal) made in processing these ores contains about 8 percent P_2O_5, and is used as a fertilizer.

Phosphatic lake beds of Eocene age are known from intermontane basins of Wyoming and Utah. The beds that contain phosphate range in thickness from less than 1 to about 6 feet and contain an average of about 2 percent P_2O_5. The maximum P_2O_5 is about 19 percent.

RESOURCES

IDENTIFIED AND HYPOTHETICAL RESOURCES

Phosphorite deposits are known throughout the world and throughout the geologic column from the Precambrian to the Holocene. Data for tonnages of identified phosphorite in tables 105 and 106 are from all possible sources. Most of the figures for the United States are from unpublished data of the U.S. Geological Survey, including information from R. L. Detterman (written commun., 1972) for Alaska. Tonnages are computed in different ways for different deposits in the United States. For the unconsolidated phosphate sands of the Atlantic Coastal Plain, they are computed on the basis of recoverable product that contains a given percent BPL (bone phosphate of lime). In Tennessee, reserves are computed as tons of rock that contain a certain percent P, and in the Western United States tonnage is phosphate rock, in the ground, of a given percent P_2O_5. Percent P_2O_5 times 2.185 equals percent BPL [equals $Ca_3(PO_4)_2$], and percent P_2O_5 times 0.436 equals percent P.

Tonnages for the United States shown in table 105 are in metric tons of rock that contain more than 24 percent P_2O_5, and total tons for the Eastern and Western United States are changed to metric tons of percent P to conform with the tonnage figures for other countries of the world in table 106.

Tonnage estimates are fairly good for the United States, Africa, the Near East, and the Pacific Islands, but it is almost certain that the estimates are low, and perhaps very low, for Latin America and Australia. The resource estimates for Asia are probably low because of lack of detailed data, particularly for China.

SEDIMENTARY PHOSPHORITE

UNITED STATES

Hypothetical resources for the United States shown in table 105 are those for which reasonable

TABLE 105.—*Phosphate resources of the United States*

[In metric tons of rocks containing more than 24 percent P_2O_5]

	Identified resources [1]	Hypothetical resources [2]
Eastern United States		
Atlantic Coastal Plain:		
Florida (Polk, Hillsborough).	1.6×10^9	700×10^6
Florida (Manatee, Hardee, DeSoto).	500×10^6	1×10^9
North Florida-South Georgia.	300×10^6	1.5×10^9
River pebble	------	50×10^6
Hardrock	50×10^6	1×10^9
North Georgia	------	1.6×10^9
South Carolina	------	500×10^6
North Carolina	2×10^9	9×10^9
Total Atlantic Coastal Plain (rounded).	4.4×10^9	15.3×10^9
Tennesse, Kentucky, Alabama	80×10^6	100×10^6
Others (Arkansas, Iowa)	26×10^6	16×10^6
Total phosphate resources, Eastern United States.	4.5×10^9	15.4×10^9
Total, tons of phosphorus.	0.59×10^9	1.69×10^9
Western United States		
Idaho, Montana, Utah, Wyoming (Phosphoria Formation).	6.0×10^9	8.7×10^9
Utah (Mississippian rocks)	------	16×10^6
Alaska	------	1×10^9
Others (Nevada, California)	------	10^9
Total, phosphate resources, Western United States.	6.0×10^9	9.7×10^9
Total, tons of phosphorus.	0.78×10^9	1.02×10^9
Grand total, tons of phosphorus.	1.4×10^9	2.7×10^9

[1] Identified resources: Specific, identified mineral deposits that may or may not be evaluated as to extent and grade, and whose contained minerals may or may not be profitably recoverable with existing technology and economic conditions.

[2] Hypothetical resources: Undiscovered mineral deposits, whether of recoverable or subeconomic grade, that are geologically predictable as existing in known districts.

TABLE 106.—*World phosphate resources*

[Metric tons of percent phosphorus]

	Identified resources [1]	Hypothetical resources [2]
United States	1.4×10^9	2.7×10^9
Africa: Sedimentary	3.5×10^9	6×10^9
Igneous	15×10^6	15×10^6
Near East	$.13 \times 10^9$	$.6 \times 10^9$
Latin America: Sedimentary	80×10^6	$.2 \times 10^9$
Igneous	13×10^6	10×10^6
Guano	5×10^6	Nil
Asia: Sedimentary	$.2 \times 10^9$	$.5 \times 10^9$
Igneous	$.2 \times 10^9$	$.2 \times 10^9$
Australia	$.2 \times 10^9$	1×10^9
Pacific Islands	6×10^6	3×10^6
Total (rounded)	6×10^9	9×10^9

[1] Identified resources: Specific, identified mineral deposits that may or may not be evaluated as to extent and grade, and whose contained minerals may or may not be profitably recoverable with existing technology and economic conditions.

[2] Hypothetical resources: Undiscovered mineral deposits, whether of recoverable or subeconomic grade, that are geologically predictable as existing in known districts.

amounts could be assigned. Additional hypothetical resources are probably large. Although all these resources are hypothetical, those not enumerated in table 105 are of a lower order of precision in terms of tonnage and are deeply buried, low in grade, or contain deleterious gangue minerals, and as a result they pose such different mining and processing problems that it seems logical to discuss them separately.

The principal additional hypothetical resource for the Western United States is contained in the Phosphoria Formation. Extrapolation of average thickness and phosphorus content over the entire area underlain by the Phosphoria indicates a total potential resource of about 16×10^9 tons of P. Of this amount, about 2×10^9 tons is represented by the identified and hypothetical resources shown in table 105. Subtracting this 2×10^9 tons from the total potential of 16×10^9 tons leaves about 14×10^9 tons of P that may be considered to be an additional hypothetical resource in the Phosphoria Formation. Of this latter amount, 5×10^9 tons contains more than 24 percent P_2O_5; 6×10^9 tons contains from 10 to 23 percent P_2O_5, and the rest consists of resources of low value. This resource will require new mining and processing techniques.

Additional hypothetical resources in the Eastern United States can be divided into sandy phosphorite of the Florida and North Carolina type and phosphatic carbonate rock such as the Hawthorn Formation of Florida. Phosphatic carbonate rock may contain scores to hundreds of billions of tons of phosphate particles, and as much as 10×10^9 tons of P. This material cannot be mined or processed with present methods.

Sandy phosphorite deposits of the Atlantic Coastal Plain are known from central Florida to North Carolina, and additional undiscovered deposits may be present in the subsurface as far north as Virginia. Deposits that are not known are completely and perhaps deeply buried; resources may aggregate billions of tons of pellets and hundreds of millions of tons of phosphorus.

In northern Alaska, hundreds of square miles are probably underlain by phosphorite, and the total tonnage represented would be billions of tons of rock that contain at least 10 percent P_2O_5, and thus, hundreds of millions of tons of phosphorus.

Large resources of phosphate rock exist offshore, but close to the shoreline, in the Pacific Ocean from southern California to southern Baja California and in the Atlantic Ocean from North Carolina to southern Florida.

Phosphate is present as very coarse nodules in

thin beds of shales and limestones in rocks of Ordovician, Devonian, Pennsylvanian, Permian, and Cretaceous ages in the midcontinent area of the United States. Phosphate particles are also concentrated as lag gravels at unconformities in this area. Although the amount of phosphate per unit area is small, the aggregate amount of phosphate most be large, and it is possible that some of these rocks may be mined as local sources of phosphate in the future.

LATIN AMERICA

Large tonnages of phosphate are known in the Jurassic of Peru and the Cretaceous of Colombia. The phosphate-bearing rocks may extend through Peru, Bolivia, and Ecuador into Colombia, and the deposits in most of this area represent a large hypothetical resource. Miocene rocks of the Sechura area in Peru and in Falcon State in Venezuela contain phosphorite deposits. The Miocene rocks of the western and northern coasts of South America should be examined to determine if additional resources are present. Along the Pacific Coast of Colombia the Miocene rocks are so thick that discovery of economic phosphate is not likely, but Miocene rocks in Ecuador and Peru and the northern coast, particularly in Venezuela, are thinner and may contain additional resources.

Deposits of the Florida type may be present in Upper Cretaceous and Tertiary rocks on the east coasts of continents. Deposits of this type occur in Cretaceous rocks of the Recife area in Brazil, but the potential is small because of the small area underlain by marine Cretaceous rocks. Deposits may also be present in Upper Cretaceous and Tertiary rocks along the present east coast of South America in Argentina.

AFRICA AND THE NEAR EAST

A very large area including much of the northern half of West Africa and all of North Africa and the contiguous parts of the Near East (Israel, Jordan, Saudi Arabia, Turkey, etc.), is a sedimentary basin in which the identified and hypothetical resources of phosphate are extremely large. The potential of this area is enormous. Deposits have been found in recent years in almost all parts of the sedimentary basin that have been examined. As details of the stratigraphy, structure, and paleogeography are worked out, additional deposits will probably be found. No tonnage figures have been computed, but the total resources must be much larger than the numbers shown on table 106.

ASIA

Not a great deal of specific information is available on this part of the world, but it is known that large sedimentary basins that contain rocks ranging in age from Cambrian to Cretaceous contain phosphorite deposits, and it is likely that exploration will uncover additional large reserves. The potential for this area is great.

AUSTRALIA

Australia has identified and hypothetical resources of phosphate of Cambrian age in a large sedimentary basin in the interior of the continent. The total resources in this basin probably are extremely large—several times the combined total of the identified and hypothetical resources shown in table 106.

GUANO AND RELATED DEPOSITS

Little hope remains for finding additional resources of the guano type of deposit such as typify the Pacific Islands. All the Pacific Islands have been searched, and although additional reserves may be found they will, in all probability, be small.

IGNEOUS APATITES

Additional resources of igneous apatite are at best moderate, particularly in comparison with the total resources of the sedimentary phosphorites. Reserves in undiscovered alkaline rock suites probably will be hundreds of millions of tons in maximum size; many will be much smaller. Reserves of this type might be utilized as local sources in the future, and the possibilities of finding deposits of apatite should not be overlooked.

SPECULATIVE RESOURCES

Very little in the way of truly speculative resources of phosphate remain to be found. We can refine ideas and theories of the formation of marine phosphorite, but the positions of the shelf, craton, sedimentary basins, and geosynclines are known at least in broad outline for most periods of geologic time throughout the world. Not all the prospective areas have been searched for phosphate, and sedimentary basins where phosphate is known have not all been thoroughly and exhaustively studied. New deposits, then, remain to be discovered but all are considered to belong to the hypothetical class rather than the speculative. The total amount of phosphate rock in the world, as identified or hypothetical, is potentially so enormous that the assumption that truly speculative resources are small has little meaning.

Truly speculative resources may be present in Precambrian rocks as metamorphosed marine phosphorite. Precambrian phosphorite deposits are known in several parts of the world and a study of the Precambrian should be made to determine the location of possible sedimentary basins. These basins should then be studied to determine if phosphorite deposits are present.

PROSPECTING TECHNIQUES

The geologic relations discussed earlier are the basis for prospecting, particularly in the outlining of large areas that are worthy of further examination.

Exploratory work should be concentrated on the search for marine phosphorite deposits. Deposits are very large; for example, it is estimated that phosphate in the Phosphoria Formation was deposited over an area of 135,000 square miles, and the potential resources, therefore, are correspondingly vast.

Most marine phosphorites were deposited in basins of deposition in miogeosynclines or in subsiding areas on the adjacent relatively stable platform, and deposits have been classified as either geosynclinal or platform type. The first step in prospecting is to identify the large marine sedimentary basins of deposition.

The second step is to determine whether any phosphate is present in the rocks of the basin. The typical suite of rocks associated with the deposits of phosphorite in the miogeosyncline is an invaluable aid to prospecting. The recognition of the black shale-chert-carbonate sequence in samples collected from oil exploration is a valuable clue to the location of a phosphorite deposit. Sandstone and light-colored shale and siltstone are much more abundant in the platform facies, but chert, calcareous chert, siliceous shale, and some carbonate rock are also present.

Phosphorite is not a very distinctive rock and can be overlooked or misidentified. Most phosphorites contain rounded to ovoid structureless sand-size pellets. Phosphatized bone fragments, fecal pellets, and fish and sharks' teeth are frequently found in phosphorites, and glauconite is a common accessory mineral. Any pelletal rock, particularly one that contains bone or teeth fragments, is worthy of further examination. Higher grade phosphorites may have a bluish-gray coating (phosphate bloom) on weathered surfaces, and high-grade phosphorite may also be distinguished by a fairly high specific gravity.

Phosphorite deposits are found where the rate of deposition of other clastic material is at a minimum. The phosphorite sequence, therefore, tends to be thin when compared with sedimentary sequences deposited elsewhere at the same time.

In a given basin of deposition, the phosphorite tends to be concentrated at one stratigraphic position, although the phosphorite facies may transgress time.

Phosphorite deposits may be structurally controlled. For example, phosphorite of the platform facies is deposited in structural basins on the flanks of domes or anticlines that were rising at the time of deposition. Structural controls, other than the broad geosynclinal basin, may determine the site of deposition in the deeper parts of the basin.

All marine phosphorites contain uranium in amounts that are high enough so that these rocks can be identified by gamma-ray well logging and even by aerial radiometric reconnaissance. Anomalous amounts of uranium are present in acid streams that drain phosphatic terranes, and in covered areas, such as the coastal plains of the United States, the presence of uranium in stream waters may be a clue to the presence of a phosphate deposit.

Large deposits of igneous apatite are related to alkalic rocks, particularly to carbonatites, and these rocks are related to the large rift zones. Many carbonatite deposits are now known; several contain large apatite deposits. All carbonatites and areas where they may be present should be examined for phosphate.

The only guano deposits that remain to be found are probably very small bat guano deposits in caves. Guano-related deposits, particularly those on arid coasts where there is modern dynamic upwelling of water, may remain to be found, and the possibilities should not be overlooked.

PROBLEMS FOR RESEARCH

Research is needed on a variety of problems that can be classified as recovery of byproducts, waste disposal, mining and processing, and geological.

Minor elements that might be recovered as byproducts include fluorine, vanadium, uranium, scandium, and the rare earths. Marine phosphorites, because of their vast tonnages, constitute significant resources of these elements. Pure apatite contains from 3.5 to 4 percent F; phosphorites probably average about 3 percent. All marine phosphorites contain uranium, probably substituting for calcium in the apatite lattice, in amounts ranging from 0.005 to as much as 0.05 percent; the average is about 0.01 percent. The rare earths (lanthanides

and yttrium) form a solid solution in the structure of apatite and make up from 0.01 to 0.1 percent by weight of marine apatite. Vanadium probably is concentrated in the organic material associated with phosphorites; the average vanadium content of phosphate rock in the Phosphoria Formation is about 0.03 percent and in Florida phosphate is 0.01 percent or less.

All these minor elements, except scandium, have been or are being recovered from phosphoric acid made by the wet process, and vanadium is now recovered in the course of thermal processing. Because only about one-fourth of the phosphate rock mined is made into phosphoric acid, the maximum recovery of the minor elements can only be about 25 percent. The probability of the recovery of scandium from this source seems remote. Research is needed to develop better methods of recovery of all these elements.

Recovery of some of the elements is related to reduction in air and water pollution. Fluorine, released in part as a gas in the chemical processing, cannot be allowed to escape in the effluent. Fluorine in the gas effluents is being controlled, but not all is being recovered. Research on methods of recovery of byproducts may lead to cleaner air and water effluents.

Solid wastes formed in processing, particularly the slime (—200 mesh) fraction from the deposits on the Atlantic Coastal Plain, cannot be dumped into streams and are currently impounded in dams. Breaks do occur, causing water pollution. The slime fraction is a potentially valuable fertilizer, and research on control, disposal, and possible utilization of the slime fraction is of utmost importance.

All open-pit mining, chemical processing, and disposal of mining and chemical wastes are now and will be increasingly regulated by clean air and water laws and by land reclamation laws. The phosphate mining and processing companies are reclaiming land in Florida and Tennessee and are working to solve problems of air and water pollution, but additional research is certainly needed. If there is any significant air or water pollution or ruining of land by mining in the future, legislation could force phosphate mining companies out of business and drastically change the export-import balance of phosphate trade.

Mining of phosphate rock is geared to shallow open pits and to underground mining above entry level. To utilize much of the hypothetical resources in the United States, new or different mining methods will have to be devised, and processing methods to recover the phosphate particles will also have to be changed. Much of the hypothetical resource is carbonate rock containing phosphate pellets, and the recovery methods currently used are not effective. Although minable reserves are sufficient for many years, the beginning of research on mining and processing problems should not wait until these reserves are nearly exhausted, but should be started promptly.

An additional set of chemical problems has to do with the amount and kind of trace metals present in phosphate rock. Certain minor elements are necessary for plant growth; among these are boron, copper, manganese, molybdenum, and zinc. These elements are all present in marine phosphorites, but are removed during chemical processing, only to be readded to the chemical fertilizer in about the same amount that was removed. Research is needed on methods of retaining these minor elements in chemical processing of phosphate rock.

Geologic problems are related particularly to the discovery of new ore deposits of high grade. The hypothesis that marine phosphorites were deposited in miogeosynclines at some distance from the source of clastic sediment and only at low latitudes has proved workable. Each miogeosynclinal basin should be investigated particularly with respect to plate tectonics and the paleolatitude of the basin at the time of phosphate deposition. Thus, a knowledge of paleogeography, paleolatitude, paleocurrents and wind directions, and structure within the basin at the time of deposition is all important in determining the locus of possible phosphorite deposition.

For deposits on the east coasts of continents—the Florida-type deposits—again a knowledge of structure, geography, and current and wind directions is important. These deposits are likely to be buried, and any geologic parameters that might be used to reduce the size of the target area to be drilled are of great importance.

Much remains to be learned about the chemistry of deposition of marine phosphorites. Phosphate may be precipitated chemically and biologically. The source of the phosphate might be ocean water itself, rivers entering the ocean, estuaries, the phosphatic bodies of fish and animals, or volcanic emanations onto the ocean floor, or some combination of all of these. The marine phosphorites are large; they contain billions of tons of phosphorus, and whatever the source, the phosphorus has to be available over long periods of time.

Problems of reserves would not appear to be important, in view of the extremely large identified tonnages, but phosphate is a low-unit-value commodity and shipping costs can put the material out

of reach economically, particularly to farmers in developing countries. There are, therefore, problems of developing resources in the countries where phosphatic fertilizer is needed.

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PIGMENTS AND FILLERS

By C. Ervin Brown

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ABSTRACT OF CONCLUSIONS

Mineral fillers are finely ground, generally white, mineral or rock additives that impart necessary or desirable physical properties to a product. Mineral pigments are mineral-derived powders added for the sole purpose of giving color. The functions of fillers and pigments overlap inasmuch as one of the common purposes of a filler is coloring.

The principal natural pigments are iron oxides, mainly hematite and limonite, that include various quantities of clay and some manganese dioxide. Production of natural iron oxide pigments is small and is decreasing and is being replaced by production of synthetic iron oxide from processes using scrap iron, or copperas from TiO_2 production.

The manufacture of pigments from zinc ore, from rutile and ilmenite, and from petroleum products is a major industry. Zinc oxide is the principal zinc pigment made from zinc ore. Manufacture of zinc oxide consumed 16 percent of zinc mine production in 1969, and the consumption trend is growing. Manufacture of TiO_2 pigment from ilmenite and rutile is the main use of these minerals and consumed 96 percent of titanium ore production in 1969. Production of carbon black as a pigment and rubber reinforcing agent consumed more than 98,000 million cubic feet of natural gas and 524 million gallons of liquid hydrocarbon. Together the value in sales of these three manufactured pigments in 1969 totaled $426 million.

Mineral fillers are made from many rocks and minerals, but kaolin, limestone, and talc make up about 84 percent of the total consumption. Fillers are essential components in paint, paper, plastics, pesticides, rubber, roofing, and fertilizer. Many fillers can be substituted for each other, but some have unique properties needed by certain products. The use of wollastonite as a filler is a recent innovation. More than 15 rocks or minerals are commonly used as fillers, and in 1969 more than 7,000,000 short tons of fillers valued at more than $350 million was used in the United States.

Consumption of pigments and fillers is intimately tied to the needs of a complex industrial society. The demand for these materials is expected to grow. Resource data for the basic ingredients of many pigment and filler commodities are given in other chapters of this volume.

INTRODUCTION

This report reviews the rocks, minerals, and fuels consumed in the United States for the production of pigments and fillers. It discusses (1) only the pigments made directly from minerals, metallic ores, and carbon black, made from gas and oil, and (2) only rock- and mineral-based fillers. Most natural mineral pigments and fillers are processed simply by grinding to very fine sizes. In addition some are calcined, and colored pigments are finished by mixing with white pigments to obtain desired tints.

Other pigments are manufactured from metallic ores by chemical processes, and carbon black is produced from gas and oil by incomplete combustion or petrochemical methods.

TERMINOLOGY

Fillers in the simplest sense are powders that are added to substances for some useful purpose. Although mineral fillers originally were intended to act mainly as adulterants and substitutes for more expensive compounds, their principal function now is to give some desirable or necessary property to a product. Commonly one of the many functions of fillers is to add color. Therefore, the functional field of fillers overlaps that of pigments, which in the purest sense are insoluble powders added only to color or tint. Because of the coloring function of fillers, some users refer to them as pigments. For example, in the rubber industry the finely divided clay and carbon black acting as reinforcing agents are called "rubber pigments," even though coloring is not necessarily their function. A recent paper (Kollonitsch and others, 1970a, b), in which the market for many mineral fillers is discussed, calls them "functional mineral pigments," distinct from "primary pigments" whose only function is coloring.

The paper industry, a major consumer of fillers, calls them "fillers" or "coaters" depending upon whether the filler is "loaded" among the fibers of the paper sheet or is used as a surface coating. The paint industry uses fillers to help form the paint film and to extend or spread out the more expensive pigments and hence calls fillers "extenders." The pesticide and fertilizer industries use the inert but absorbent qualities of some fillers to dilute and carry the chemicals and hence call them "carriers." This carrier-chemical combination in turn is diluted further for field application by fillers known as "diluents."

In order to avoid confusion, mineral *filler* as used in this report is synonymous with the special terms just mentioned and is a finely ground and generally inert rock or mineral powder added to give desirable or necessary physical properties to a finished product. A mineral *pigment* as used in this report is an insoluble powder added only for the purpose of imparting color, tint, or opacity to a finished product. By these definitions, a pigment is a one-purpose filler serving only to color.

NATURAL PIGMENTS

A comprehensive survey of the iron oxide pigment market in the United States and Great Britain recently appeared in the periodical "Industrial Minerals" (1971a). The principal previous study of mineral pigments was by Siegel (1960). Much of the information in the following paragraphs is from these sources.

Mining of pigments was one of the earliest mineral industries of primitive man and in America was done extensively by the Indians. Most notable among the mineral pigments are the earth colors produced by iron oxides. Some other mineral pigments are ultramarine from lapis lazuli, green earth from weathered basaltic tuffs, and a very unstable blue from azurite. Alteration of the latter might be responsible for the now green skies in some old Italian paintings (Ladoo and Myers, 1951).

Most pigments now are produced synthetically from ores or metals or as byproducts of other processes. The only important production of mineral pigment is from the natural iron oxides because they are inexpensive and available, although the market for these too is threatened by synthetic iron oxides because the consistency of color and particle size from synthetic iron oxides are more easily controlled. Increasing use of organic dyes has also cut deep inroads in the natural pigment market.

IRON OXIDE PIGMENTS

The principal iron oxide pigments are ochers, siennas, and umbers. Compositions vary widely, but limonite and hematite are the principal coloring agents. Mixed with these are various quantities of manganese oxide, clay, and in the case of Vandyke brown, organic material in the form of humates. Table 107 gives the approximate composition of earth pigments.

TABLE 107.—*Approximate composition of earth pigments, in percent*

[Adapted from Siegel, 1960]

	Ocher	Sienna	Umber
Fe_2O_3	17–60	25–75	37–60
SiO_2	35–50	10–35	16–35
Al_2O_3	10–40	10–20	3–13
MnO_2	-----	(1)	11–23
H_2O loss on ignition	10–12	15–20	10–15

[1] Small percentage.

Even though gradation of shades between ochers, siennas, and umbers is complete, the natural iron oxides can be conveniently classified according to their colors. Table 108 lists their properties, sources, and uses.

TABLE 108.—*Natural iron oxide pigment colors and sources*

Colors	Trade names	Principal world sources	United States sources	Comment
Yellow and yellow-brown.	Yellow ocher, Roman ocher, Chinese yellow.	South Africa; France.	Cartersville, Ga. Henry, Va., Eastern Pa.	Permanent, opaque.
Red and red-brown.	Persian red, Spanish red.	Ormuz Island, Persian Gulf; Jaen, Spain.	Mather iron mine, Marquette County, Mich.	Permanent, opaque.
Brown	Raw umber, named for Umbria, Italy.	Cyprus	Imported	Permanent colors; Raw umber is calcined to remove organic material and to oxidize the ferrous oxide to Fe_2O_3 and produce burnt umber.
Dark brown	Burnt umber	do	Imported	Do.
Dark yellow-brown.	Raw sienna	Sienna, Italy	Imported; (ochers from Georgia are sometimes called sienna).	Transparent, therefore can be used for staining; raw sienna calcined to produce burnt sienna.
Bright reddish brown.	Burnt sienna	do	do	Do.
Brown-black	Vandyke brown.			Contains humates; fades to gray when exposed to bright light.

Micaceous iron oxide, a pigment not included in tables 107 or 108, is a special-purpose pigment used to make anticorrosive paint and is not used for its color. Austria is the principal source, and about 8,000 tons per year is mined from large continuous deposits. An unspecified quantity is imported by the United States, although this type of paint is not commonly used here (Am. Paint Jour., 1970). In England, some railway bridges painted in 1944 with this pigment have not rusted except where scratched by the inevitable graffiti (Indus. Minerals, 1971a).

Most mining of iron oxide pigments in the United States is on a small scale. The largest production is from the Mather mine in Marquette County, upper Michigan, where it is a coproduct of iron mining. About 25,000 tons of hematite, about 1 percent of the annual mine production, is produced there for the pigment, paint, and chemical industries. Other production is from small mining operations mainly in Georgia, Virginia, and Pennsylvania. The deposits in these States are limonite and ocherous material that has been leached from pyrite-bearing sedimentary rocks and redeposited by ground water in fractures or in the residual soil. Deposits in Georgia are in fractures and fault zones in Cambrian quartzites; and in eastern Pennsylavnia, residual deposits are associated with Paleozoic limestones and quartzites. The deposits of residual limonite in Virginia are in two belts, one along the west slope of the Blue Ridge Mountains and the other associated with Cambrian quartzites in Pulaski County (Siegel, 1960). These deposits at one time were the sites of small-scale iron-mining operations, but now they produce only pigment.

IRON OXIDE PIGMENT MARKET IN THE UNITED STATES

Although the demand for pigments is increasing, the sale of natural iron oxides for pigments is declining. In 1969, finished pigments in the amount of 142,900 short tons valued at $32.3 million were sold; in 1970, sale of 40,800 short tons of crude natural pigments was $362,000. Imports of refined and synthetic iron oxides were 33,431 short tons, close to the amount of mine production in the United States (Fisher, 1969). Synthetic iron oxides are taking an increasingly large share of the world market. Imports into the United States include about half synthetic material.

COMPETITIVE MATERIAL

Although synthetic iron oxide pigment has replaced natural iron oxide in much of the market, the use of the natural material continues steadily in some areas. The synthetic material is produced mainly in two ways—one, by precipitation of ferrous hydroxide from an iron salt solution; and the other, by calcination of hydrated ferrous sulfate (copperas). The first process uses scrap iron as a raw material, and the second uses byproduct ferrous sulfate from the production of titanium dioxide from ilmenite. No iron ore is used as raw material by the synthetic iron oxide industry. West Germany leads the world in this industry with exports alone totaling 125,600 short tons in 1970 (Indus. Minerals, 1971a). The United States produced 70,507 short tons in 1969. Not all synthetic iron oxide goes to the pigment industry; an unspecified amount is used to produce ferrites which are increasingly being used for their magnetic and electrical properties.

PROSPECTING AND FIELD TESTS

Almost any ocherous soil, vein, or deeply colored red, yellow, or brown sedimentary rock is potentially an iron oxide pigment. Most of these deposits are diluted with clay and other impurities; consequently their tinting strength is low. A simple test in the field for tinting strength is to grind the ma-

terial in a mortar and mix it with 10–20 times its weight of powdered ZnO and then to compare with commercial pigments treated similarly to disclose the tinting strength. Dilution with white ZnO is called "letting down" the pigment and is done to obtain desired shades in finished pigments. Another test is to determine the effect of particle size on the color. Each pigment has an optimum particle size, close to 1 micron, below which light scattering causes some undertones to be lost. On the other hand particle size above 2 microns causes a rough paint film. Tests for other properties, such as oil absorption, hiding power, and mass color are also important and are described by Siegel (1960).

RESOURCES OF IRON OXIDES FOR PIGMENTS

Because synthetic and byproduct iron oxides are rapidly replacing the use of natural oxides, speculation here about resources of the natural oxides that are discussed in the iron chapter of this volume is probably not significant. However, it is well to remember that red and yellow ocherous materials, such as in gossans, have a market, if they occur in sufficient quantity to be recovered easily. Ladoo and Myers (1951, p. 348) describe an operation in which pigment is extracted from acid coal-mine drainage:

> . . . In Pennsylvania, where pigment recovery is attempted, logs and rocks are placed in the discharge of mine waters pumped from the mine. These obstacles agitate the water and aerate the solution, introducing oxygen and thereby accelerating the precipitation of the iron oxide. Economical recovery can be obtained only where there is a substantial tonnage within a few hundred feet of sufficient thickness to permit movement by ordinary shoveling . . . The yellow mud is shoveled from the stream, which may be diverted, or in some cases from the floor of the mine tunnel, with care to avoid contamination by soil or coal . . .

Acid mine drainage charged with iron salts is one of the many pollution problems facing us today. Perhaps a more efficient process than that described above of aerating and recovering the precipitate from such water might provide a salable resource while aiding in cleaning the streams of iron in these problem areas.

MISCELLANEOUS PIGMENTS

Graphite, magnetite, and some carbonaceous slates have been used for black pigments, but the market for these materials as pigments is very small, with graphite the leading commodity. In 1969, graphite in the amount of 182 tons valued at $28,000 was consumed for paints and polishes. Magnetite is one of the few minerals that grinds to a black powder, but statistics on its current consumption as a pigment are not available.

MANUFACTURED PIGMENTS

Zinc ores, ilmenite and rutile, and fossil fuels are used as raw materials in the production of ZnO, TiO_2, and carbon black, respectively—all major pigments.

ZINC PIGMENTS

Production of zinc compounds used for pigments in 1969 consumed 120,700 short tons of zinc ore of which 89,900 tons was domestic and represented 16 percent of total zinc mine production in the United States. The percentage used for pigments has been steadily increasing, and this use should continue as an important market for zinc ores.

The principal zinc compounds used as pigments are zinc oxide, zinc chloride, zinc sulfate, leaded zinc oxide, and lithopone, a coprecipitate of zinc sulfide and barium sulfate. Shipments of zinc oxide and zinc sulfate, produced mainly from zinc ore, have increased sharply as zinc oxide production has increased since 1960. The other zinc compounds are produced mainly from slab zinc and scrap and as byproducts. Consumption of zinc pigments other than zinc oxide and zinc sulfate is decreasing (Moulds, 1969).

Zinc oxide is used mainly in the manufacture of white rubber products such as white sidewall tires. The rubber industry consumed 116,000 tons of zinc oxide in 1969, representing 53 percent of lead-free zinc oxide production (Moulds, 1969). The manufacture of photosensitive copying paper consumed 27,600 tons of zinc oxide, and the manufacture of paint, particularly alkyd-latex paint used 25,200 tons. Other zinc compounds used as pigments were consumed mainly by the paint industry.

The total value of zinc pigments produced in the United States from zinc ores in 1969 was about $77.5 million out of about $80 million for zinc pigments from all zinc materials. During the year the United States imported an additional 23,500 tons of zinc pigments, an increase over previous years, and these imports were valued at $4.5 million (Moulds, 1969). Resources and other aspects of the zinc industry are discussed in the chapter of this volume on zinc.

TITANIUM DIOXIDE

Titanium dioxide, a very important pigment, is made from ilmenite, rutile, and titanium slag that is the residue after smelting ilmenite. All titanium dioxide for use as pigment is recrystallized after chemical treatment of the mineral concentrates. The resulting TiO_2 is synthetic rutile or anatase or a mixture of the two. Both have very high reflect-

ance; and because of rutile's high index of refraction, the rutile-type pigment has a very high opacity or hiding power, making it valuable for paint or as a paper coating.

Titanium dioxide for pigment is the principal product of titanium ores in the United States. Of 1.29 million tons of concentrates mined in 1970, 1.24 million tons or 96 percent was made into titanium pigments. The paint and paper industries consumed 76 percent of this and the remainder was divided among rubber, floor covering, textiles, ink, ceramics, and plastics manufacture and exports. The value of titanium pigments shipped in 1969 was $333 million for 652,000 short tons (Noe, 1970); data for 1970 are not available. Other aspects of titanium and its resources are covered in the chapter of this volume on titanium.

CARBON BLACK

Carbon black is a nearly pure micron-sized carbon produced from natural gas or liquid petroleum by incomplete combustion or by thermal decomposition under carefully controlled conditions that determine the particle size, structure, and physical properties. Although carbon black is virtually a black pigment, its main use is as a reinforcing agent in tire rubber. As a pigment, it is used in ink and paint. The plastics industry used only a small amount of carbon black to color plastics until it was discovered that a larger percentage greatly improved the resistance of polyethylene to becoming brittle from sunlight aging. Now as much as 50 percent carbon black is added to polyethylene cable coverings for this purpose (Kelley and Harper, 1970, p. 66), another example of the overlapping functions of pigments and fillers.

A direct relation exists between the expanding rubber industry and the growing consumption of carbon black. Other uses of carbon black, especially in inks and paints, do not show a similar increase in growth. Production of carbon black in 1969 was 1.48 million short tons valued at $215 million. About 98,251 million cubic feet of natural gas and 524.4 million gallons of liquid hydrocarbons were consumed in its production. A process having an efficiency of 1–5 percent and using natural gas to produce "channel blacks" is giving way to much more efficient processes as the price of natural gas climbs (Kelley and Harper, 1970). Exports in 1969 were 98,100 tons of carbon black, which represented a 25.4 percent decrease from 1968 despite increased foreign production of tires. Expansion of U.S.-owned and foreign-owned carbon black companies close to sources of foreign gas and oil accounts for this decrease in our exports (Kelley, 1969, p. 247). Imports in 1969 were 3,000 tons of specialty carbon blacks.

OUTLOOK FOR PIGMENTS

The demand for pigments is directly related to the manufacture of paint, printing inks, and coloring matter for rubber and plastics. These products are all voraciously consumed by a suburbia- and automobile-oriented society such as that of the United States. The demand for pigments will grow as population and gross national product increase.

The demand for natural mineral pigments, such as iron oxide, however, is being supplanted by synthetic pigments because consistency of the manufactured product is more easily controlled. This trend toward the synthetic probably will continue although the market for good natural pigments will undoubtedly continue. Recovery on a large scale of iron oxide pigments as a byproduct of treatment of acid mine water is an intriguing possibility for the future.

Production of ZnO, TiO_2, and carbon black is increasing, and because these pigments are basic in the manufacture of paints, rubber, and plastics their demand will expand with the national growth.

MINERAL FILLERS

Mineral fillers are finely ground, generally inert rock or mineral additives used for the purpose of giving necessary or desirable physical properties to a finished product. Almost any rock could be pulverized and serve some of the many functions of a filler; however, several rocks and minerals satisfy the rigid physical specifications of filler products particularly well and are the backbone of mineral filler consumption, which reached 7 million tons in 1969. The principal filler materials are kaolin, limestone, diatomite, carbon black, talc, asbestos, mica, barite, fuller's earth, pyrophyllite, and wollastonite. Many of these have specific properties, such as the fibrous particle shape of asbestos, that makes them uniquely suited for certain uses. Others, however, such as kaolin, talc, and pyrophyllite, can be substituted for each other for some purposes; their use than also depends on availability, transportation, and cost of mining and beneficiation. Because of these additional factors and the ability of some filler minerals to be substituted for others, attention should be paid by geologists, working in districts with convenient transportation to industrial parts of the country, to the potential suitability of white-grinding fairly soft, chemically inert rocks and minerals for use as mineral fillers.

INDUSTRIAL FILLER USES AND REQUIREMENTS

Of the varied industries using mineral fillers, each has specific requirements for the fillers it consumes. Much of the following information on the use of fillers was obtained from Cummins (1960).

ASPHALT OR BITUMINOUS COMPOSITIONS

Fillers are used in asphalt composition for road paving, roofing, reservoir linings, tile, joint sealers, battery boxes, and many other products to increase the viscosity, melting point, resistance to mechanical stress, hardness, or resistance to weathering. In many products the filler is loaded to nearly 50 percent, and in items such as asphalt tile, filler is the major component. In asphalt products the filler particles form an interlocking skeletal lattice which provides high viscosity and strength. Therefore, fibrous or platy particle shape is a more important property of the filler for asphalt products than are color and smoothness.

PAINT

Fillers used in paint are known as extenders because they hold more expensive pigments in suspension and upon drying form the paint film which supports and spreads out the pigment. Here the desirable mineral properties are platy or fibrous particle shape, smoothness and extreme fineness, high reflectance, and low oil absorption. The latter is important because most paints use oil and resins as vehicles, and therefore more pigment filler can be used per volume of oil and drying time is reduced if the oil is not absorbed by the filler particles. Desirable qualities sought through the proper choice of extender are consistency of film formation, film toughness, resistance to weathering, flatness, opacity, and a reduction of costs through using less prime pigment. Generally a mixture of extenders is used in order to get the desired paint qualities. With the increased use of water-based latex paints some consideration is given to the alkalinity of the filler in order to increase corrosion resistance. Most fillers are inert, but some, such as wollastonite, produce alkaline suspensions (Andrews, 1970), which are desirable to decrease "rusting through" of nail heads and rusting of paint cans and are compatible with pigments that would react if used in low pH suspension. Uniform fineness of particles is extremely important for paint extenders, because coarse particles show on thin paint films. For most uses, fillers must pass a 325-mesh screen, but as paint extenders they are ground to micron sizes, and techniques to grind particles finer are actively sought.

PLASTICS

Plastic floor tile has long been a major consumer of asbestos and other fillers. Inasmuch as the plastics industry is rapidly expanding and developing new products, many more types of mineral fillers are being used. The consumption of talc, wollastonite, and other fillers is rapidly expanding for this use because of the strength, electrical and heat resistance, and whiteness of these fillers. Carbon black is used to increase resistance of polyethylene to sunlight aging although it was used initially as a pigment. Properties desired from fillers in plastics are color, strength, electrical and heat resistance, increased melting point, stiffness, decreased brittleness, and low shrinkage. Many plastic products contain nearly 50 percent filler, which is responsible for most of the physical properties of the products.

RUBBER

The rubber industry is a major consumer of fillers used as reinforcing agents to increase tear resistance, abrasion resistance, stiffness, heat dissipation, and electrical resistance and to intensify color. Much research has been done by the rubber industry to understand the actual physical function of filler particles in rubber (Huber Corp., 1955; Cummins, 1960). Particle size required for rubber fillers demands nearly 100 percent passing through a 325-mesh screen. Grit particles tend to cause tearing and excess wear of cutting and extruding equipment. The percentage of loading fillers depends upon the desired quality of the finished rubber product, and a wide range up to more than 50 percent is common. For white rubber products color is important, and barite, zinc oxide, and titanium oxide are used with kaolin. Barite is also used to increase specific gravity, as in rubber mallets. Carbon black is the major reinforcing pigment used by the rubber industry. Kaolin also is an important rubber filler and is used to increase hardness and abrasion resistance. Very fine grained kaolin produces hard rubber, hence is known as "hard clay." "Soft clay," a coarser clay, allows rubber to remain soft.

PAPER

Another major consumer of fillers is the paper industry. This industry uses mineral fillers in two ways, one as a filler or loader, in which filler mixed with bonding agents fills the voids between the felted cellulose and textile fibers to be rolled out as the paper sheet, and the other as a surfacing material or coating where whiteness, opacity, and gloss are desired. Pigments and mineral fillers, for example flux-calcined diatomite with TiO_2, are often used in

combination for coating. In this combination, the diatomite is a pigment extender (Cummins, 1960). Chalk and Harris (1968) give a thorough discussion of the uses of mineral fillers by the paper industry.

PESTICIDES

Mineral fillers are used as diluents and carriers for insecticides and fungicides. Because the toxic elements cannot be distributed efficiently or effectively in the concentrated form, they must be diluted in liquids or dusts to insure proper distribution and a concentration that will not have deleterious effects on the host, yet will destroy the harmful organisms. The toxic chemicals are first mixed with a mineral powder known as a carrier to make a concentrate that is simple to store, ship, and handle prior to use in the field. Mineral fillers suitable for carrier use, like diatomite, fuller's earth, and some clays, are highly absorptive. These must be dispersible in liquids for sprays and must be inert and compatible with the toxicant involved. Fineness and low abrasiveness are important to avoid clogging and excess wear of nozzles.

This carrier-pesticide mixture usually is further diluted for application from aircraft or ground equipment. The filler used for this application is known as a diluent. It must be of fine particle size and have low abrasiveness but need not be highly absorptive like the carrier. A good pesticide carrier also acts as a grinding aid in preparation of some pesticides, and as a conditioning agent for the diluent, so that dust is free flowing but will stick to the plant surface for maximum exposure to the harmful organisms (Cummins, 1960).

One interesting aspect of diluents and carriers is that some mineral dusts cause very high mortality rates on some insects and larvae when applied even without the toxic chemicals. Apparently these mineral dusts clog the digestive and respiratory systems (Huber Corp., 1955).

OTHER USES

Much mineral filler is used as a carrier and diluent for fertilizer, for most of the same reasons as in pesticides. Fillers also have miscellaneous uses in adhesives, joint cement, and many other products, each of which demands specific physical properties of the filler.

FILLER MINERALS

Cummins (1960, tables 1 and 2) listed 19 minerals and mineral products, not including wollastonite, that commonly are used for fillers in the United States. Table 109 is an adaptation of his table 1 showing major uses for the principal filler minerals. Resources and the export-import relation for most of these minerals are discussed in other chapters in this volume and consequently are not discussed here. Pumicite, rock dusts, slate, and vermiculite are included by Cummins, but are excluded here because they are minor fillers or because very few data are available concerning their production and consumption. Further information about vermiculite is in the chapter on light-weight aggregates in this volume. Some fillers, such as rock dusts, are byproducts of other milling or mining activities.

Excluding carbon black, 55 percent of the total tonnage of minerals or rocks consumed as fillers is kaolin. Limestone ranks second with 23 percent and of the remaining 22 percent, talc leads with 6 percent of the consumption, and many minor fillers make up the remaining 16 percent.

The trends of domestic demand for seven major fillers for the past 12 years are shown in figure 63. Kaolin, fuller's earth, and talc show increasing

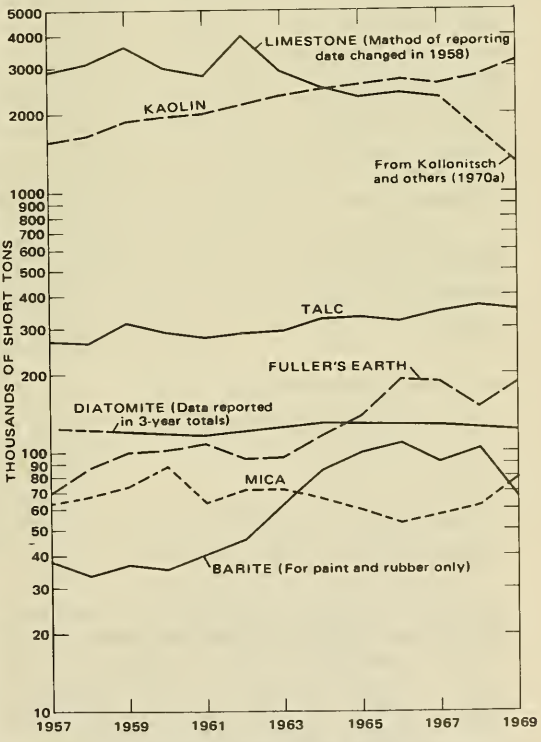

FIGURE 63.—Consumption trends of seven major mineral fillers in the United States, 1957–69.

TABLE 109.—*Properties, value, and industrial utilization of the principal mineral fillers used in the United States in 1969*

[×, percentage unknown]

Mineral filler	Distribution by end use (In percent, if known)								Percentage of total commodity consumption	Approximate value (in thousands of dollars)	Distinguishing properties	Approximate tonage used in United States for filler (in thousands of tons)	Remarks
	Paint	Rubber	Paper	Fertilizer	Pesticides	Plastics	Roofing	Other unidentified uses					
Asbestos	—	—	—	—	—	>75	×	×	25	20,000	Nearly all uses based on fibrous nature.	200	Filler uses take mainly "fines" and "shorts." (See "Asbestos" chapter.)
Barite	75	20	—	—	—	—	—	5	4	>4,000	Highest density filler; inert, light colored.	66	About 80 percent of the world's annual production is used for heavy drilling mud. (See "Barite" chapter.)
Bentonite and other clays, excluding fuller's earth and kaolin.	—	—	—	—	7	—	—	93	0.5	500	Absorbent	28	Not an important filler; mainly an insecticide diluent. (See "Clay" chapter.)
Carbon black	×[1]	90±	—	—	—	5	—	×	95	200,000	Extremely fine particle size; only black filler.	1,480	Excellent rubber reinforcing agent. Also a pigment.
Diatomite	×	—	×	×	×	×	—	×	20	7,200	Inert or reactive opaline silica depending upon whether calcined; skeletal silica particles.	120	Used in raw state, milled or calcined for fillers. Large reserves. (See "Diatomite" chapter.)
Fuller's earth	—	—	—	—	95	—	—	5	20	5,000	Absorbent; cost low	187	Mainly used for floor sweeping compound, rotary drilling muds, and decolorizing agent. (See "Clay" chapter.)
Gypsum	×	—	×	—	×	—	—	—	<5	3,000±	Low cost; soft	100±	Minor filler mineral; used raw or calcined. (See "Evaporites and brines" chapter.)
Kaolin	4	12	75	3	<1	2	—	4	66	67,500	White, low oil absorption; abundant, low cost.	3,164	Most important filler mineral, principal paper filler, important rubber filler. (See "Clay" chapter.)
Limestone	×	×	—	×	×	×	—	×	5	22,000	High brightness; low oil absorption; availability good and cost low.	1,300	Cheapest filler; has low oil absorption and good color. Main filler for putty, caulking, and sealants. (See "Limestone and Dolomite" chapter.)
Mica, ground	37	9	×[2]	—	—	<1	52	×	62	5,100	Micaceous structure; high dielectric strength, spangled sheen to wallpaper.	79	Scrap mica, including some phlogopite and biotite. Mica and sericite schists are resources. (See "Mica" chapter.)
Perlite	×	—	—	—	—	×	—	×	1	220	Light-weight; vesicular structure.	5	Not an important filler. Mainly used for plaster and concrete aggregate and filtering aid. (See "Light-Weight Aggregate" chapter.)
Pyrophyllite	×	×	—	—	×	—	×	×	65±	1,000±	Inert, soft, high brightness.	111	Statistics reported with talc in U.S. Bur. Mines Yearbooks; about 27,000 tons used for ceramics.
Silica, ground	×	×	—	—	—	×	—	×	Small	?	Hardness; low oil absorption.	?	For paint extender in deck paints, for high abrasive use.
Talc	47	7	16	—	16	×	8	×	40	14,000	Inert, soft, high brightness; some varieties fibrous or platy.	350	Some grades contain much tremolite, anthophyllite, or serpentine. (See "Talc" chapter.)
Wollastonite	×	×	—	—	—	×	—	—	25±	200	White, acicular-fibrous; low oil absorption; alkaline suspension.	5	Mainly used in ceramics; newest important filler mineral.
Total	—	—	—	—	—	—	—	—	-----	350,000	----------	7,200	

[1] Used as a pigment.
[2] Used in wallpaper.

consumption as fillers; consumption of barite as a filler has decreased in the last few years after it showed a spectacular increase starting in about 1960. As a filler, diatomite has experienced no increased demand, and mica has a very erratic demand. Limestone, which along with kaolin is the major filler, has had a strong decrease in demand as a filler, although information is incomplete because the U.S. Bureau of Mines since 1967 has reported limestone data differently, and the 1969 figure for limestone as a filler (Kollonitsch and others, 1970a) is not explained.

Although most filler minerals are discussed elsewhere in this volume, wollastonite, a mineral relatively new to the filler industry, is not discussed elsewhere and is reported on here.

WOLLASTONITE

Wollastonite ($CaSiO_3$) an acicular white mineral, is used mainly for wall tile and other ceramic products. It is an excellent ceramic material in that it can be fired rapidly because no H_2O or CO_2 must be driven off. The resulting ceramic does not absorb water and is resistant to thermal shock and brittleness. Although wollastonite is mainly used by the ceramic industry, its use as a filler is becoming much more common. The finished filler is brilliantly white, fibrous, and an excellent paint extender because its fibrous character suspends the pigment and prevents the accumulation of hard sediment in the paint can. Wollastonite also forms a strong paint film that weathers well. The filler is chemically stable, and suspensions of wollastonite are alkaline with a pH of about 10 (Andrews, 1970). This alkalinity has an advantage in paints like polyvinyl acetate that decompose in time, forming acetic acid. The alkaline suspension neutralizes the acid and prevents corrosion of the paint can.

The rubber industry uses wollastonite as a semireinforcing filler in nonblack rubber goods. The plastics industry uses it in thermosetting and thermoplastic casein resins and in asphalt and vinyl floor tiles. Wollastonite filler has high opacity and has been experimented with as a filler and coater for paper. For these uses, however, it apparently cannot compete with kaolin, which is less expensive.

Most wollastonite is found in contact metamorphic zones between calcareous and intrusive rocks. In the United States it was mined for mineral wool as early as the 1930's from a small deposit in Kern County, Calif. A much larger deposit at Willsboro, N.Y., along the contact of the anorthosite mass in the northeastern part of the Adirondack Mountains, was developed in the early 1950's, and material mined from there since 1953 is used in an ever-increasing number of products. Total world production of wollastonite has been not over 50,000 tons, and four-fifths of this has come from the New York deposit. The other principal producers are Mexico and Finland. Andrews (1970) has a complete and comprehensive report on wollastonite, its uses, and resources throughout the world. The periodical "Industrial Minerals" (1969b, and Whitmer, 1969) also presented a thorough study of wollastonite.

Although most of the U.S. production of wollastonite is from the deposit in New York, the mineral is still mined in Riverside County, Calif., where recovery is mainly for decorative stone. In 1966, however, some mining for industrial wollastonite was begun from the California deposits, but production since then apparently has been small.

Arizona, Nevada, Utah, and the Virgin Islands are also cited by Andrews (1970) as containing notable occurrences of wollastonite.

World identified resources of wollastonite amount to more than 60 million tons, and hypothetical resources are three times that according to Andrews (1970, p. 2). An appraisal of resources by nations has not been made.

MISCELLANEOUS FILLERS

Several other minerals and rocks such as Portland cement, gypsum, rock dust, ground slate, and phosphorite are locally and occasionally used as fillers. A small quantity of feldspar also has been used in the past few years as an extender in paint and a filler in rubber.

OUTLOOK FOR FILLERS

The market for mineral fillers is intimately dependent on the needs of a complex industrial society. The demand has steadily grown and should continue as a result of expansion of paper, plastics, paint, rubber, and other industries. No great spurts have occurred in the consumption of any one filler, and in fact consumption of some has declined; nevertheless, the overall demand has continued with many small advances as new products and uses are devised. This steady growth in demand will undoubtedly continue in the United States. Because industries requiring fillers generally seek a local source for filler material to avoid high transportation costs, any light-colored inert rocks with low-cost transportation to industrial areas should be evaluated for their potential use as a filler to help satisfy this expanding demand.

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UNITED STATES MINERAL RESOURCES

PLATINUM-GROUP METALS

By Norman J Page, Allen L. Clark, George A. Desborough and Raymond L. Parker

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ABSTRACT OF CONCLUSIONS

The United States produces only 1–2 percent of the platinum metals that it uses and is therefore virtually totally dependent upon foreign supplies; accordingly, the hypothetical and speculative resources in Alaska, Montana, California, Oregon, and Washington are of some interest for possible future platinum production. More precise evaluation of these resources will not be possible without improved analytical techniques for the platinum-group metals at concentrations less than 10 parts per million. The current lack of such techniques greatly hinders geological, geochemical, petrological, and mineralogical research necessary to evaluate the potential platinum resources.

INTRODUCTION

Platinum, palladium, iridium, osmium, rhodium, and ruthenium are the platinum-group metals. Platinum and palladium are the most abundant of this group, but all these metals are essential to modern industry where their applications are based on their catalytic properties, electrical conductivity, and resistance to chemical corrosion, heat, and oxidation. About 1.3 million ounces per year of platinum-group metals (Ageton and Ryan, 1970) are consumed in the United States (1) by electrical manufacturers as electrical contacts in high-precision instruments and insoluble anodes for metallurgical processing; (2) by the chemical industry as catalytic gauze for oxidation of ammonia and the manufacture of nitric acid; (3) in petroleum refining as a catalyst to produce high-octane gasoline; (4) in dental and medical devices; (5) in decorative arts and jewelry; and (6) as spinnerettes used in manufacturing glass and synthetic fibers.

The United States produces only 1–2 percent of the platinum metals that it uses and is therefore almost totally dependent upon foreign supplies. The major sources are the Republic of South Africa, U.S.S.R., Canada, and Colombia.

EXPLOITATION

Platinum metals have a long and somewhat erratic history of exploitation beginning in the 7th Century B.C. when a single forged grain of platinum was used as a hieroglyphic character by an Egyptian artisan to decorate an etui. It was reported to have been used

by Indians in Colombia before the arrival of the Spanish. Although Colombian placers were first described by Scaliger (1557, p. 323–324), mining of them did not begin until 1778, soon after the first chemical work on platinum was done. Until 1823, Colombia was the only source of platinum metals, but soon after the 1822 discovery of platinum in placers in the Ural Mountains, Russia became the world's greatest producer, which it has remained except during 1936–61.

Platinum placers were mined as early as 1885 in Canada, but lode deposits were not mined for platinum until 1919, when platinum metals began to be recovered from the nickel-copper deposits of the Sudbury district. By 1936, Canada had become the principal producer. In 1923 platinum lodes were discovered in Transvaal, Republic of South Africa, and in the following year in the Bushveld Complex. By 1956 and 1957, output from these lodes outstripped Canadian production. Russia ranked third for a long time, but as the Uralian placers became depleted, lodes were found in Siberia that by 1961 again raised Russian output to first rank, with the Bushveld and Transvaal second and Canada third. In 1929, platinum placers were discovered in Alaska, and since 1934, Alaska has ranked fifth in world production, and Colombia fourth. The Witwatersrand district, South Africa, a producer of osmiridium, ranks sixth.

Through most of the first quarter of the 20th Century, placer deposits furnished the world's supply. The discovery of lodes in South Africa, Canada, and Siberia so altered the situation that in 1971 these three countries produced more than 98 percent of the world's output. Production records have not been accurately kept, but production has amounted to about 63,685,000 ounces through 1971.

The geologic occurrence of platinum-group metals as lodes or placers dictates that copper, nickel, gold, silver, and chromium will be either coproducts or byproducts in the recovery of the platinum metals and that platinum will be largely a byproduct. For example, about 1 ounce of platinum-group metals is recovered for each 35 tons of copper produced (Ageton and Ryan, 1970) from domestic ores. Because a larger part of the domestic production is a byproduct of copper mining, environmental effects or problems mainly are those directly related to the mining and refining of copper. Indeed, a suggested use of platinum catalysts is as a potential pollution control of nitrogen oxide fumes.

GEOLOGIC ENVIRONMENT

GEOCHEMISTRY

The crustal abundance of the platinum-group metals (Wright and Fleischer, 1965) is poorly known, owing to the low concentration of these elements and inaccurate analytical techniques. Mason (1958) estimated crustal abundances as follows: Pt, 5 ppb; Pd, 10 ppb; and Ir, Os, Rh, and Ru, 1 ppb each. Useful equivalents are: 1 ppb (part per billion) = 0.001 ppm (part per million) = 0.000032 oz per ton (troy ounce per ton).

The complex, unique, but poorly known chemical nature of the platinum-group elements in geologic environments prohibits accurate generalizations regarding their distribution and geochemical cycle. The highest concentrations of the platinum elements are generally in igneous rocks that formed at high temperatures, an indication that the platinum metals are indigenous to the earth's mantle. Certain conditions of high temperature and (or) high sulfur partial pressure may result in mobilization and concentration of the platinum-group elements. Because of their high specific gravity, the platinum metals are concentrated by surficial or hydrologic processes to form placer deposits.

MAJOR MINERALS OF THE PLATINUM ELEMENTS

The platinum metals are major constituents of several metallic alloys and a number of minerals with anions of sulfur, arsenic, antimony, bismuth, and tellurium. As Wright and Fleischer (1965) listed most of the known platinum minerals and references to their mineralogy, this report considers only those in domestic occurrences (table 110). With the exception of occurrences in the Stillwater Complex, Montana, virtually all the known platinum-group minerals in the United States come from placers, in which the material ranges from microscopic-size grains to nuggets several centimeters in the largest dimension. Mertie (1940, p. 72) observed that most nuggets and grains are composed of two or more minerals intergrown to form the grains, and recent microscopic and electron microprobe studies have validated this observation.

CLASSIFICATION OF DEPOSITS

The major workable deposits of platinum metals occur with nickel-copper and copper lodes associated with mafic and ultramafic rocks and as platinum alloys in placers. Mafic and ultramafic rocks form at least three distinctive types of igneous complexes (Jackson and Thayer, 1972): (1) Stratiform—floored, tabular complexes consisting of vertical repetitions of well-layered rock sequences with cumulus textures, that are intrusive into Precambrian shields or into basaltic terranes of any age; (2) Concentric—roughly cylindrical, zoned complexes

TABLE 110.—*Principal minerals and domestic occurrences of the platinum-group metals identified by electron microprobe or X-ray diffraction analysis*

Name or approximate composition	Locality	Reference
Alloys or metals		
Ferroplatinum (Pt, Fe, Ir, Os, Ru, Rh, Pd, Cu, Ni).	Goodnews Bay, Alaska	This study.
	Humbodlt County, Calif	Do.
	Trinity River, Calif	Snetsinger (1971a).
	Stillwater, Mont	Page (1971); Page and others (1971).
	Port Orford, Oreg	This study.
Iridium-ruthenium-osmium	Goodnews Bay, Alaska	Leonard and others (1969).
	Humboldt County, Calif	This study.
	Trinity River, Calif	Snetsinger (1971a).
Osmium	Goodnews Bay, Alaska	This study.
Osmium-iridium	Goodnews Bay, Alaska	Do.
	Beegum Creek, Calif	Spencer (1971).
	Hay Fork Creek, Calif	Do.
	Humboldt County, Calif	This study.
	Antelope-Pony dist., Madison County, Mont.	Do.
	Port Orford, Oreg	Do.
Sulfides		
Laurite, $(Ru, Ir, Os)S_2$	Goodnews Bay, Alaska	Leonard and others (1969).
	Port Orford, Oreg	This study.
	Stillwater, Mont	Page (1971); Leonard and others (1969).
Erlichmanite, OsS_2	Trinity River, Calif	Snetsinger (1971b).
Cooperite, PtS	Humboldt County, Calif	This study.
	Stillwater, Mont	Do.
Unnamed, (Ir, Rh, Pd)S	Goodnews Bay, Alaska	This study.
Arsenides and antimonides		
Mertieite, $Pt_5(Sb,As)_2$	Goodnews Bay, Alaska	Desborough and others (1972).
Sperrylite, $PtAs_2$	Humboldt County, Calif	This study.
	Stillwater, Mont	Howland and others (1936).
	Goodnews Bay, Alaska	J. R. Mertie, Jr., (written commun., 1972).
Rodian sperrylite, (Pt, Rh, Ni, Pd) $(As, S)_2$.	Humboldt County, Calif	This study.
Osarsite, $(Os, Ru(AsS)$	Gold Bluff, Calif	Snetsinger (1972).

consisting of layers formed by sedimentary, metamorphic, and igneous processes, that are intruded into metamorphic rocks of eugeosynclinal orogenic belts; and (3) Alpine—irregularly shaped discordant complexes consisting of discordant lenticular layers of rocks with tectonite fabrics, that are tectonically emplaced in eugeosynclinal orogenic belts and island arcs.

Layered deposits or contact-metamorphic deposits associated with stratiform and concentric complexes are the major sites of platinum-lode deposits. Examples are the Merensky Reef in the stratiform Bushveld Complex, South Africa (Cousins, 1969), and the deposit of the Noril'sk district, Siberia (Mertie, 1969), which could be classified as a concentric mafic complex.

Platinum placers consist of unconsolidated alluvial deposits in present or ancient stream valleys, terraces, beaches, deltas, and glaciofluvial outwash, and in lithified placers of similar origin. The placer metals are commonly derived from mafic and ultramafic rocks, but may come from nearby sources in sedimentary rocks, having ultimately been derived from mafic and ultramafic rocks during a previous erosion cycle. As the densities and sizes of platinum alloys are generally similar to those of alluvial gold, some platinum metals, when present, are recovered from gold placers.

A domestic source of platinum-group metals is as a byproduct of refining copper from porphyry and other copper deposits and from lode and placer gold deposits, although the grade is extremely low. Other minor lode sources are in copper-gold contact-metamorphic deposits, copper deposits associated with syenitic rocks, and gold-quartz veins. Relatively small potential deposits exist domestically; such ores represent only a minor platinum resource, but serve to indicate the range of geologic environments.

STRATIFORM COMPLEXES

The Stillwater Complex (Hess, 1960; Jones and others, 1960; Jackson, 1961; Page and Nokleberg, 1970) of Precambrian age in southwestern Montana contains several potential platinum lodes. Platinum, palladium, and rhodium are concentrated in the chromitite zones, but individual samples vary widely in contents and ratios of these three platinum metals (Page and others, 1969; 1971). The lowermost chromitite, the A zone, averages 0.10 oz/ton and attains a maximum known value of 0.60 oz/ton of Pt+Pd+Rh. Stibiopalladinite, sperrylite, cooperite, platinum-iron alloy, and laurite are the only platinum minerals identified (Page, 1971); they occur as inclusions (average diameter 5–10μ) in chromite and in interstitial sulfides. Chromium shows the strongest correlation with platinum metals, V a moderate correlation, and Ni, Co, and Cu a lower correlation. Platinum metals occur in the greatest amounts where the oxidation ratio of chromite is lowest. This relation suggests that less oxidizing conditions favoring crystallization of chromite also favored the concentration of platinum metals from the magma. Platinum metals, though in lesser amounts, also occur below the A zone in the basal zone and are associated with massive and disseminated copper-nickel sulfides. Small amounts of platinum metals have also been reported from disseminated sulfide

layers in the upper gabbroic rocks of the complex (Howland and others, 1936; Page and Jackson, 1967; Page and others, 1969).

CONCENTRIC COMPLEXES

The concentrically zoned ultramafic complexes and associated mafic bodies of southeastern Alaska contain only one known platinum lode, developed by the Salt Chuck mine. Both platinum and palladium were recovered as a byproduct of copper mining. The ore minerals occur as small masses and disseminations in pyroxenite, gabbro, and gabbro pegmatite (Mertie, 1969, p. 76). The platinum metals are closely associated with bornite and chalcopyrite. The form in which the platinum metals occur is not known, but sperrylite has been identified in one specimen.

Potential platinum lodes may exist within the concentrically zoned ultramafics, as shown by anomalous concentrations of platinum as high as 29 ppm in the chromite-bearing dunite core of the ultramafic complex at Union Bay.

ALPINE COMPLEXES

Alpine complexes may or may not represent potential platinum resources, judged on relatively few modern analyses. Eighteen dunites and harzburgites from Burro Mountain, Calif., average 12.8 ppb Pt, 3.7 ppb Pd, and <5 ppb Rh (Loney and others, 1971). Analyses of dunites and harzburgites from Red Mountain and New Idria in California, and of similar rocks from Twin Sisters and Cypress Island in Washington, average <10 ppb Pt, <4 ppb Pd, and <5 ppb Rh. Chromites from these occurrences average slightly higher—36 ppb Pt, 10 ppb Pd, and 9.5 ppb Rh (Page, 1969).

OTHER MAFIC-ROCK ENVIRONMENTS

Minor platinum-metal deposits associated with copper, nickel, and gold in mafic and ultramafic rocks are probably insignificant in terms of platinum-metal resources but illustrate other environments where platinum metals are found. For example, deposits in the Bunkerville district, Nevada (Beal, 1965), have a reported range in grade of 0.14 to 0.25 oz/ton. Another example is in the Revais Creek district, Montana, where 0.23–0.54 ppm Pt and 0.10–0.79 ppm Pd (eight samples from the Copper King deposit) are found in a gold-silver-copper ore that consists of chalcocite, bornite, and chalcopyrite. The ore is in a hornblende gabbro dike and in the Ravalli Group (Precambrian) that it intrudes. The Rambler and Centennial mines, Wyoming, produced a small amount of platinum-group metals with a grade between 1 and 1.3 oz/ton from deposits of irregular shape in mafic igneous and metamorphic rocks (Mertie, 1969; Theobald and Thompson, 1968).

PLACERS

Platinum-group metals occur in many placers within the United States. Minor amounts of the platinum group have been recovered from the gold dredges of California and from the gold placers of Oregon, Washington, Montana, Idaho (Logan, 1919), and Alaska, but significant amounts have been produced only from the placers of the Goodnews Bay district, Alaska.

Platinum-metal-bearing placers of the Goodnews Bay mining district occur in two paystreaks in the valley of the Salmon River (Mertie, 1969, p. 80). Total production from 1927 to 1969 is believed to have been considerably more than half a million troy ounces, with a maximum output exceeding 30,000 ounces in 1938 (Mertie, 1969, p. 79). The weighted mean percentages of metals mined from 1936 to 1970 are 82.31 percent platinum, 11.28 iridium, 2.15 osmium, 0.17 ruthenium, 1.29 rhodium, 0.38 palladium, and 2.24 gold.

The platinum metals of these placers are contained mainly in two alloys. The major alloy is ferroplatinum; microprobe analyses by G. A. Desborough gave the results shown in table 111. The minor alloy consists dominantly of iridium and osmium, with small amounts of platinum, and still smaller amounts of ruthenium and rhodium. In addition to these two alloys, minute amounts of five platinum minerals—cooperite, laurite, sperrylite, mertieite, and a yet-unnamed iridium-palladium sulfide (table 111)—have been identified.

TABLE 111.—*Composition, in weight percent, of ferroplatinum in 50 placer grains from Goodnews Bay, Alaska*

	Mean (standard deviation)	Range
Pt	86.1 (1.8)	82.7–88.6
Fe	9.3 (.6)	8.2–11.2
Ir	2.26 (1.70)	.1– 2.0
Rh	.9 (.5)	.1– 2.0
Pd	.65 (.3)	.1– 1.4
Cu	.7 (.3)	.1– 1.1
Os	.3 (.3)	.1– .8
Ru	.1	.1– .1

MINOR OCCURRENCES

Platinum metals are associated with alkalic intrusive rocks (syenites) that have copper mineralization, but very little is known about this environment. The Copper Hill mine, La Plata mining district, Colorado (Eckel, 1949), is in an ore zone of chalcopyrite that contains platinum and palladium.

(A recent analysis of chalcopyrite-bearing dump material by L. T. Riley and O. M. Parker, U.S. Geol. Survey, gives 0.37 ppm Pt and 0.45 ppm Pd.) Analyses by the U.S. Bureau of Mines from samples in the small area immediately surrounding the glory hole of the Copper Hill mine averaged 1.87 percent Cu, 0.49 ounce Ag, and 0.005 ounce platinum metals. Other recognized minerals are hematite, magnetite, pyrite, garnet, ankerite, quartz, and fluorite. The ore zone seems to be the result of intense late-stage fracturing and subsequent replacement of the rock with orthoclase and ore minerals, mainly chalcopyrite, in a highly sericitized and feldspathized porphyry.

Another chalcopyrite deposit, in a syenite near Cooke City, Mont., contains 0.5 to 10 ppm Pt, 0.15 to 3 ppm Pd, and as much as 0.04 ppm Rh (U.S. Geol. Survey, 1971). This deposit also is associated with widespread potassium metasomatism and veining of potassium feldspar.

The Boss mine, Nevada (Hewett, 1931), is a typical example of the gold-quartz association. (For other examples, see Mertie, 1969.) About 1,000 ounces of platinum metals were recovered from a pipe-shaped gold-copper-quartz deposit in a minor fault zone.

RESOURCES

IDENTIFIED AND HYPOTHETICAL RESOURCES

Identified and hypothetical resources estimates are given in table 112. The numbers of ounces of platinum-group metals should be viewed with extreme caution and recognized as estimates of order of magnitude. Total known and potential platinum-group metal resources obviously must not exceed the total production to date and the amount in the earth's crust. The lower limit is 63,685,000 ounces; the upper limit, using Poldervaart's (1955) estimated mass of the earth's crust and Mason's (1958) average abundance of platinum-group metals, must be much less than 1.5×10^{16} ounces. Ageton and Ryan (1970) estimated the world reserves at 424 million ounces—probably a conservative estimate.

The estimates of subeconomic resources of platinum-group metals in the concentric zoned ultramafic complexes of Alaska are based on published reserves of 500×10^6 tons of titaniferous magnetite at the Klukwan deposit (averaging 0.0027 oz per ton platinum metals) and 500×10^6 tons of titaniferous magnetite at the Snettisham deposit (average 0.0027 oz per ton platinum metals). Additional areas of titaniferous magnetite associated with both of the bodies have a total potential of 3.5×10^9 tons (averaging 0.0027 oz per ton platinum metals).

TABLE 112.—*Identified, hypothetical, and speculative resources of platinum-group metals, in million troy ounces*

IDENTIFIED RESOURCES [1]		
Summary data from Ageton and Ryan (1970)		
World (total)		424
United States (total)		3
Goodnews Bay, Alaska	.3	
Salt Chuck, Alaska	.012	
South Africa		200
U.S.S.R.		200
Canada		16
Colombia		5
Data from various sources		
Alaska:		
Snettisham		4.55
Klukwan		7.55
Goodnews Bay		6.8
Lodes	1.3	
Bays	5.0	
Beaches	.5	
Lituya Bay beaches		.06
Gold placers		.016
Porphyry copper		.06
Copper deposits		.002
Montana, Stillwater Complex:		
Basal zone		2.4
Chromites		2.2
California, Tertiary gravels		.008
Western United States, porphyry copper		[2].002
United States, minor occurrences		.002
South Africa, Bushveld Complex		656
Rhodesia, Great Dyke		[1]100
South Africa. Witwatersrand		[3].075
HYPOTHETICAL RESOURCES [4]		
Alaska:		
Concentric complexes		35
Porphyry copper		.15
Gold deposits		.032
Montana, Stillwater Complex: Basal zone		150
Conterminous United States:		
Gold placers		.057
Chromite deposits, excluding Stillwater Complex		.002
SPECULATIVE RESOURCES [5]		
Alaska:		
Continental shelf		4
Kenai-Chugach ultramafic belt		?
Fairbanks-Livingood ultrafafic belt		?
Southeastern Alaska ultramafic belt		?
Porphyry copper, Alaska Range		?
Alkalic rocks, Seward Peninsula		?
California-Oregon-Washington:		
Continental shelf		?
Beaches		?
Antarctica, Dufek intrusive		?
Brazil, Goias serpentine belt		?
Worldwide:		
Syenitic and alkalic rocks		?
Basaltic rocks		?

[1] Identified resources: Specific, identified mineral deposits that may or may not be evaluated as to extent and grade, and whose contained minerals may or may not be profitably recoverable with present technology.
[2] From Ageton and Ryan (1970).
[3] Based on Ageton's (1970) reserve estimates of gold for South Africa and on Cousins' (1972) ratio of osmiridium to gold produced.
[4] Hypothetical resources: Undiscovered mineral deposits, whether of recoverable or subeconomic grade, that are geologically predictable as existing in known districts.
[5] Speculative resources: Undiscovered mineral deposits, whether of recoverable or subeconomic grade, that may exist in unknown districts or in unrecognized or unconventional form.

The estimates of identified platinum-group metals in the basal zone of the Stillwater Complex, Montana, are based on published reserves (Dayton, 1971) of ore tonnages and the existence of a 25-mile-long zone, averaging 300 feet in width and workable on the average to 2,000 feet downdip with a probable average of 0.5 ppm platinum-group metals. Similar estimates were made for the chromitite, using average platinum-group-metal content of the A, G, and H zones.

The 250-mile-long Merensky Reef of the Bushveld Complex, South Africa, has been mined locally downdip 6,000 feet, with an average stoping thickness of 28.5 inches (Mertie, 1969). The grade ranges from 0.25 to 0.35 oz per ton. If a grade of 0.25 oz per ton persists throughout the reef's extent and the reef were mined to 10,000 feet, about 656 million ounces of platinum-group metals would be available in addition to the 200 million ounces estimated by Ageton and Ryan (1970, p. 657). Mertie (1969) implied that only 70 miles of reef could be productive under present economic conditions, and so our estimate represents a large proportion of subeconomic resources.

The other area of identified resources is in the Goodnews Bay mining district and the contiguous offshore areas. Exploration there by mining companies has shown the presence of anomalous amounts of platinum metals in Goodnews Bay and in the beaches and offshore sediments. A recent study by Allen L. Clark (unpub. data) defined anomalous platinum-metal zones within the nearby Red Mountain ultramafic mass.

The hypothetical resources (table 112) of Alaska are large, primarily because all the ultramafic bodies studied to date (Clark and Greenwood, 1972) contain anomalous amounts of platinum (table 113). In addition, the concentrically zoned complexes of southeastern Alaska are geologically very similar to the platiniferous bodies of the Ural Mountains, Russia, and therefore may have a comparable potential. One ultramafic body at the Salt Chuck mine yielded a large amount of platinum and palladium as a byproduct of copper mining, indicating the likelihood of undiscovered economic concentrations.

TABLE 113.—*Concentrations, in parts per million, of platinum, palladium, rhodium, and iridium, southeastern Alaska*

Name of area	Pt conc.		Pd conc.		Rh conc.	Ir conc.
	Max.	Ave.	Max.	Ave.	Max.	Max.
Duke Island	0.200	0.037	0.140	0.033	0.010	----
Union Bay	29.000	.093	.200	.023	.062	0.215
Blashke Islands	.020	.010	.020	.010	----	----
Salt Chuck	.160	.057	2.900	1.010	----	----
Klukwan	.100	.046	.100	.040	----	----

Other belts of ultramafic rocks exist in Alaska, and where studied, have all been found to contain anomalous amounts of platinum metals. Frequently, placer mining for gold has recovered small amounts of platinum metals from streams draining these ultramafic belts.

T. P. Thayer (U.S. Geol. Survey, 1957) estimated chromite reserves in alpine ultramafic rocks and in beach sands in Oregon, California, and Washington; these deposits, in turn, are estimated to contain 0.03 ppm platinum-group metals and could, then, yield 1,660 hypothetical ounces of platinum-group metals as a byproduct.

The U.S. Bureau of Mines (1967) estimated the potential production of gold from placers in California, Oregon, Washington, and Montana as 81,068,000 ounces. Comparison of gold and platinum production figures and estimates by Logan (1919) and Pardee (1934) suggests that for each ounce of gold about 0.0007 of an ounce of platinum-group metal is recovered. This suggests that there are 57,000 ounces of potential platinum metals in these placers.

SPECULATIVE RESOURCES

Limited knowledge of the geochemistry and geologic environments of platinum metals makes it difficult to speculate about potential resources. With the assumption that platinum metals are derived from the mantle, then one may speculate that any igneous rocks that have a direct known or postulated origin in the mantle may contain resources of platinum metals (table 112). Ore deposits associated with some basalts or with some types of alkalic rocks and their associates—for example, carbonatites—might be worth investigating for platinum potential. Of course, known but unexplored stratiform mafic and ultramafic complexes, such as the Dufek in Antarctica (Ford, 1970), and known but inadequately explored belts of ultramafic rocks, such as the central Goiás Precambrian serpentine belt in Brazil (White and others, 1971), would have to be included as speculative resources. As noted by Wright and Fleischer (1965), platinum metals are sometimes concentrated by late-stage magmatic and hydrothermal processes and therefore pegmatites may be a potential source of platinum.

After erosion and weathering, platinum metals apparently act in two ways: (1) as heavy minerals and (2) by dissolving. Any locality in which heavy minerals are concentrated from potential platinum-bearing terranes, and localities where salines are found in drainage basins draining potential platinum ter-

ranes should be investigated as speculative residences of platinum metals.

More specifically, integration of regional geologic trends and the minor occurrences of platinum-group metals throughout the gold placers of Alaska allows one to speculate that large resources of platinum metals exist in Alaska. If such resources exist, they will be associated with three major ultramafic rock belts, a major porphyry copper province, and the alkalic rocks of the Seward Peninsula.

The three major ultramafic belts—the Southeastern Alaska, Kenai-Chugach, and Fairbanks-Livingood belts—are only partly explored, and new ultramafic areas will undoubtedly be found in each of these three belts. In addition, large areas of Alaska, at present unmapped, may contain additional ultramafic belts. Therefore, with the high potential for undiscovered ultramafic host rocks and the wide areal distribution of platinum metals in placer deposits associated with the ultramafic belts, the potential for large platinum metal resources is very high.

The common occurrence of platinum metals with porphyry copper deposits indicates that potentially large resources of platinum metals may exist throughout the 500-mile extent of the Alaska Range. Locally within the Alaska Range, porphyry copper deposits exist, and the potential for the discovery of several new districts is very good.

A belt of alkalic rocks approximately 200 miles long exists in the eastern Seward Peninsula. To date no analyses for platinum metals have been made, but the potential of this area is very high, in light of platinum metals associated with similar types of rocks.

PROSPECTING TECHNIQUES

Prospecting for platinum metals has been, and continues to be, rather intuitive. Perhaps the most successful approach has been to look for placer accumulations of platinum metals by standard panning techniques and then attempt to find the lode source. After location of the lode source, normally a mafic or ultramafic body, prospecting has been concentrated on locating the oxide- and sulfide-rich zones with which the platinum metals are commonly associated.

Recent work by Clark and Greenwood (1972) on the zoned ultramafics of southern and southeastern Alaska has shown strong correlations of platinum and palladium with specific major and trace elements and rock types (table 114). Although the correlations are consistent within an individual complex, they differ between complexes. Similar correlations between rock and mineral types and trace elements were noted by Page, Riley, and Haffty (1969; 1971).

TABLE 114.—*Correlations of maximum platinum-palladium concentrations, southeastern Alaska*

Name of area	Host rock	Associated oxide or sulfide	Elements showing positive correlation with Pt and Pd
Duke Island	Hornblendite	Magnetite, chalcopyrite.	Fe, V
Union Bay	Dunite	Chromite, magnetite.	Fe, Cr
Blashke Islands	Hornblendite	Magnetite, chalcopyrite.	Fe, Ni
Salt Chuck	Pyroxenite, gabbro, gabbro pegmatite.	Bornite, chalcopyrite.	Cu
Klukwan	Pyroxenite	Magnetite, ilmenite	Fe, V

Analytical studies have also shown that the stratiform and concentric ultramafic complexes are more likely to contain platinum lodes than the alpine type. Therefore, once a favorable type of ultramafic body has been defined, the following procedure is most effective: (1) sample and analyze all rock and mineral phases for platinum metals and associated trace major elements such as Fe, Cr, Ni, V, Ti, and Cu; (2) establish correlations between platinum metals and rock elements; and (3) define and sample areas with highest correlation parameters as probable lode sources. When utilizing this technique, it should be remembered that the lode zone being sought is normally very thin, even though it may extend for a long distance. Therefore any sampling done perpendicular to the layering must be close spaced.

Recent studies by Cousins (1969, 1972) and Fuchs (1972) show that both platinum and palladium may be readily leached in the zone of weathering in source rocks as well as in placers. This fact suggests that regional geochemical prospecting techniques designed to locate soluble and transported platinum and palladium may be an effective way to locate potential platinum metal lode sources. Soil sampling for platinum metal lodes may also be effective if one looks for the more stable platinum metals such as Os, Rh, Ir, and Ru. An attempt was made by Rudolph and Moore (1972) to define lode sources using geobotanical prospecting; they reported that species of *Eritrichium chamissonis, DC.* contained up to 4.8 ppm platinum collected from the Red Mountain ultramafic mass at Goodnews Bay, Alaska. Other attempts to use this method have been unsuccessful (J. B. Mertie, written commun., 1972).

Platinum metals do, however, occur in many diverse geologic settings, particularly with copper deposits, and the techniques of exploration for these

other deposits should be indirectly applicable in the search for potential platinum resources.

PROBLEMS FOR RESEARCH

Whereas base metals can be located by geochemical prospecting of stream sediments and soils and by geobotanical and geophysical methods, the discovery of platinum metals nearly always requires a direct chemical analysis of samples of the ore deposit. Nevertheless no laboratories can yet provide accurate results for all six platinum-group elements using a single analytical method, when these metals are present at concentrations less than 10 ppm. Methods do exist for Pt, Pd, and Rh down to the low part-per-billion range (Haffty and Riley, 1968).

Indirect techniques needed to help locate platinum metals will require research into the chemical and physical behavior of platinum metals in the weathering and transportation cycles. Research on the geophysical parameters of platiniferous zones in known occurrences is also necessary as a prelude to developing useful geophysical prospecting techniques. Trace-element studies of platinum metals are also necessary to define pathfinder elements.

A complete study of the nature and behavior of platinum metals should also be undertaken with the purpose of defining presumably unknown geological environments where these metals may be found.

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UNITED STATES MINERAL RESOURCES

RARE-EARTH ELEMENTS

By JOHN W. ADAMS and MORTIMER H. STAATZ

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ABSTRACT OF CONCLUSIONS

The rare-earth metals, which include yttrium and the lanthanides, consist of a group of geochemically related elements that have become of increasing economic interest, largely on the basis of their physical rather than their chemical properties. Their greatest present use is in petroleum-cracking catalysts, but they are also extensively used in the glass and ceramics industries, in iron and steel production, and in the manufacture of electronic devices.

Some members of the group are relatively abundant in the earth's crust, but minable concentrations are uncommon. Bastnaesite, a rare-earth fluocarbonate, and monazite, a rare-earth phosphate, are the two important ore minerals. Bastnaesite is mined extensively from carbonatite in California, and monazite is recovered largely from placer deposits in various parts of the world. The rare earths are present in many other minerals, either as essential constituents or as substituted constituents. Apatite is a common host of the substituted constituents and is a source of rare earths as a byproduct of fertilizer manufacture in Europe.

The large reserves of bastnaesite in California make the United States self-sufficient in the lanthanide elements, but no such high-grade source of yttrium is known. Potential domestic resources capable of meeting projected requirements, however, are available.

INTRODUCTION

The rare-earth group of metals, also called the lanthanide elements, comprises 15 elements having atomic numbers 57 through 71. These are lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), and lutetium (Lu). One of these, promethium, is best known as an artificially produced element, although its occurrence in minute trace amounts in natural materials has been reported. In addition to the lanthanides, yttrium (Y), with atomic number 39, is generally classed with the rare earths because of its chemical similarities and geochemical affinities. The rare-earth group is divided into the cerium subgroup, or "light" rare earths, which consists of the first seven lanthanide elements listed (lanthanum through europium), and the yttrium subgroup, or "heavy" rare earths, which consists of yttrium and the last eight lanthanide elements listed (gadolinium through lutetium).

USES

The rare earths are the basis for a small but increasingly important industry that had its origin about 100 years ago when rare earths were used as a minor constituent in thorium gas mantles. The annual domestic consumption of rare-earth oxides is now more than 10,000 tons, compared with about 2,000 tons a decade ago. Most of the rare earths used are in the form of oxides, chlorides, or fluorides of one or more of the major members of the cerium subgroup—that is, cerium, lanthanum, neodymium, and praseodymium—derived from bastnaesite or monazite ores. Yttrium and the less abundant lanthanides, notably europium, are used to a lesser extent but, because of their higher cost, contribute disproportionately in dollar value to the industry. Yttrium has been extracted from several source materials including residues from the processing of Idaho euxenite for niobium, Canadium uranium ores, monazite, and xenotime. The rarer lanthanides may be obtained from bastnaesite ores or from any of the sources of yttrium just mentioned.

Uses for the rare earths are diverse and are based largely on the physical rather than the chemical properties of the group. The major use at present is in petroleum-cracking catalysts, in which rare earths replace sodium in a synthetic zeolite structure. Adoption of this type of catalyst began about 1964 and has contributed greatly to the expansion of the rare-earth industry. Next in importance is the use of rare earths in the glass and ceramic industries, where they are used in the form of oxides, chlorides, or fluorides for a variety of purposes, including polishing materials, opacifiers, colorizers, and decolorizers, and as inhibitors of radiation coloration in television-tube glass. Rare earths are used in both ferrous and nonferrous metallurgy, sparking alloys, and carbon-arc electrodes. Research into the properties of individual rare-earth elements has led to many new uses within the past decade. These have been based largely on their optical and luminescent characteristics related to their unusual atomic structure. Applications are in phosphors for color-television tubes and high-intensity lighting, in lasers, and in synthetic rare-earth garnets for microwave systems. Permanent magnets of exceptionally high coercive strength are being made using intermetallic compounds of rare earths and cobalt, of which $SmCo_5$ appears to be the most promising. These and other uses of the rare earths are more fully discussed by Parker and Baroch (1971) and by Cannon (1972).

New uses for rare earths undoubtedly will follow technological advances in many fields, and by the same token, some present uses will become obsolete. Research into catalysts for automobile exhaust emission control has indicated that compounds of rare-earth elements and certain transition elements, notably the compound $LaCoO_3$, hold considerable promise (Libby, 1971). Adoption of such catalysts would, of course, create an unprecedented demand for the rare earths, as well as for cobalt. Another potential application of rare earths that could greatly increase their usage is in the removal of phosphates from wastewater. Discharge of phosphate-bearing wastewater into streams and lakes is a major cause of the "death" of bodies of water through eutrophication, and only a small percentage of the phosphate is removed by present water-treatment plants. A method that offers almost complete removal by precipitation as a rare-earth phosphate was described by Recht, Ghassemi, and Kleber (1970).

AVAILABILITY

The rare earths are comparative newcomers among the elements used by industry, and the extent to which they are employed by a country reflects to some extent the degree of sophistication of its technology. If rare earths were to become unavailable, the effect on our present standard of living would not be catastrophic because, in most applications, the rare earths are merely replacing other materials that are less effective for the particular purpose. Without rare earths we would have inferior color television, camera lenses, and cigarette-lighter flints; far more serious might be the effects felt in the fields of glass manufacture, communications, ceramics, and the iron and steel industry, and less gasoline would be produced per barrel of crude oil.

Since the development of the bastnaesite deposit at Mountain Pass, Calif., the United States has become largely self-sufficient in rare-earth resources. Bastnaesite, however, is a cerium subgroup mineral, and it contains only a very small percentage of yttrium and the yttrium subgroup lanthanides. Recent demands for these elements, notably yttrium, have been met by their extraction from (1) residues from the processing of Idaho euxenite for niobium, (2) monazite from beach placer deposits, which is chiefly imported, and (3) residues from Canadian uranium mills. Of these, the Idaho residues are now exhausted, and the recovery of rare earths by Canadian uranium mills has been discontinued. The present requirements for yttrium are small, however, and appear to be adequately met by stocks on hand and by existing sources. The United States, therefore, is a potential exporter of the light

rare earths and an importer of the heavy rare earths, although the latter role is one of economics rather than one of necessity, inasmuch as large undeveloped resources of yttrium are present in domestic deposits, particularly in apatite-magnetite bodies and western phosphate rocks.

GEOLOGIC ENVIRONMENT

GEOCHEMISTRY

The lanthanides and yttrium are lithophilic elements and are most commonly found as phosphates, carbonates, or silicates. In the geologic environment they are commonly trivalent with the exceptions of cerium, which may be in a Ce^{+4} state, and europium, which may be present as Eu^{+2}. The lanthanides are unique in their electronic arrangement in that with increase in atomic number, electrons are added to an inner (4f) level rather than to outer levels. This arrangement results in the general chemical similarity of elements in the group, but it also gives them some unusual physical properties. One consequence of inner-level backfilling is the so-called lanthanide contraction, a progressive decrease in the ionic radius of the trivalent lanthanide ions from lanthanum to lutetium. Ionic-radius relationships are very important in rare-earth geochemistry in that they are fundamental to natural mechanisms by which the elements in this rather cohesive group may become separated from one another. These mechanisms, which depend on ionic size, basicity differences, coordination effects, solubility characteristics, and stability of complexes, are able, individually or collectively, to effect a natural fractionation of the rare earths to a remarkable degree (Adams, 1969).

The actual abundance and distribution patterns of the lanthanides and yttrium in terrestrial and extraterrestrial materials have been the subject of much recent research facilitated by the use of activation-analysis techniques (Haskin and others, 1966; Herrmann, 1970). From the analytical data many attempts have been made to estimate the rare-earth content and distribution both in the whole earth and in its several crustal units, of which the continental crust has the greatest significance when we are considering the resources and geochemistry of the elements in the accessible parts of the earth. Taylor's (1964) abundance data for the rare earths in the continental crust are plotted in figure 64 to show their distribution pattern. Judging from Taylor's estimates and those of Lee and Yao (1965), the average rare-earth content of the continental crust is somewhat less than 200 ppm (parts per million).

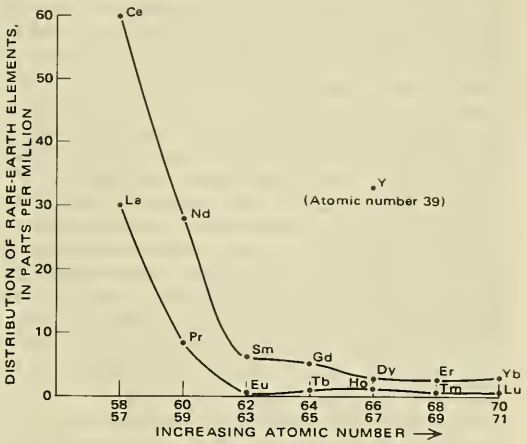

FIGURE 64.—Crustal abundance of the rare-earth elements. Even-odd pairs of elements are arranged in increasing atomic number along the abscissa of the graph, and abundance, in parts per million, is plotted along the ordinate. The upper curve connects lanthanides of even atomic number; the lower, their odd-numbered neighbors. Yttrium has been arbitrarily placed with dysprosium and holmium because of their similarity in ionic radii.

The rare-earth content and distribution pattern of the different rock types vary considerably. Haskin and Frey (1966, p. 310) noted that the absolute rare-earth content of intrusive rocks generally increases from ultramafic rocks, through mafic and intermediate rocks, to the silicic granites. Various sedimentary rock types, although they may differ appreciably in their total rare-earth content, show mutually similar distribution patterns, which indicates that fractionation is minimal during sedimentation.

Table 115 shows the rare-earth content of various

TABLE 115.—*Rare-earth content of various rock types*

[From Haskin and Frey, 1966]

Rock type	Number of samples	Rare-earth content (ppm)
North American shales	Composite of 40.	235
Ocean sediments	8	102–271
Graywackes	5	70–195
Carbonate-bearing sedimentary rocks.	8	16–159
Sandstones	5	52–126
Basalt	Composite	174
Granite (G–1)[1]	(2)	334
Russian granites	3	225–475
Gabbros	3	28–123

[1] Wesberly, R.I.
[2] Number of samples not known.

rock types from the data of Haskin and Frey (1966). Even this limited sampling illustrates that the amount of rare earths present can vary widely within a single rock type. Rare-earth contents greater than those shown in the table have been found in both sedimentary and igneous rocks; marine phosphorites, for example, commonly have a high rare-earth content, and some granites and syenites may contain more than 1,000 ppm.

A significant part of the rare-earth content of rocks may be present in "carrier" minerals such as apatite, sphene, zircon, and the ferromagnesian minerals. Plagioclase feldspar may be enriched in europium (Haskin and Frey, 1966, p. 313). These minerals, as well as the specific rare-earth minerals, contain preferential rare-earth assemblages which may vary with their geologic environment (Fleischer and Altschuler, 1969).

When rare-earth minerals are liberated from their host rocks by weathering, they may accumulate in the soil or be transported from their original site by running water. Heavy, resistate minerals such as monazite may accumulate in fluviatile or seabeach placers or become incorporated in sediments depositing offshore. As the minerals are largely insoluble under surface-weathering conditions, there is very little release of rare-earth ions for the development of secondary minerals.

An interesting geochemical cycle for monazite was proposed by Overstreet (1960, 1967) to explain its relative abundance in highly metamorphosed rocks, and its virtual absence in those where the grade of metamorphism was low. He suggested that detrital monazite in the original sediment becomes unstable during initial metamorphism and breaks down, the rare earths entering other structures. As the intensity of metamorphism increases, monazite is again formed and reaches its maximum abundance in rocks that have undergone the most intense metamorphism. Monazite commonly contains 3–8 percent of thorium, and, as noted by Overstreet, the thorium content is also influenced by the degree of metamorphism, being greatest in monazite from the most highly metamorphosed rocks.

MINERALOGY

The rare earths are essential constituents of over 100 mineral species and are present through substitution in many more. Only a few, however, have been found in sufficient concentration to be used solely as rare-earth ores; some others are recovered primarily for one or more other elements, with rare earths as a byproduct.

A partial list of rare-earth-bearing minerals and their general compositions is given in table 116. Of these, monazite and bastnaesite are the most important by virtue of their abundance, high rare-earth content, and amenability to processing and are the two basic ore minerals used by industry. Xenotime, the yttrium phosphate, is also used, but to a minor extent. Byproduct rare earths have been produced from apatite in Finland, euxenite in the United States, loparite in the U.S.S.R., and from uraninite and brannerite in Canada.

Monazite is a common accessory mineral in some igneous and metamorphic rocks and in ancient and modern placers. Most economic concentrations of

TABLE 116.—*A partial list of rare-earth-bearing minerals*

Mineral	Composition
Oxides:	
Cerianite	CeO_2.
Fluorides:	
Fluocerite	$(Ce,La)F_3$.
Fluorite, cerian (yttrocerite)	CaF_2 + dominantly Ce subgroup.
Fluorite, yttrian (yttrofluorite)	CaF_2 + dominantly Y subgroup.
Carbonates and fluocarbonates:	
Ancylite	$(Ce,La)_4(Sr,Ca)_3(CO_3)_7(OH)_4 \cdot 3H_2O$.
Bastnäsite	$CeFCO_3$.
Doverite	$CaY(CO_3)_2F$.
Parisite	$2CeFCO_3 \cdot CaCO_3$.
Synchisite	$CeFCO_3 \cdot CaCO_3$.
Silicates:	
Allanite	$(Ca,Ce,Th)_2(Al,Fe,Mg)_3 \cdot Si_3O_{12} \cdot (OH)$.
Cenosite	$Ca_2(CeY)_2Si_4O_{12}CO_3H_2O$.
Cerite	$(Ce,Ca)_2Si(O,OH)_5$.
Gadolinite	$Be_2FeY_2Si_2O_{10}$.
Huttonite	$ThSiO_4$.
Stillwellite	$(Ce,La,Ca)BSiO_5$.
Thalenite	$Y_3Si_2O_7$.
Thorite	$ThSiO_4$.
Thortveitite	$(Sc_2Y)_2Si_2O_7$.
Phosphates:	
Apatite [1]	$Ca_5(PO_4)_3F$.
Brockite	$(Ca,Th,Ce)PO_4 \cdot H_2O$.
Florencite	$Ce,A'PO_4)_2(OH)_6$.
Phosphates—continued:	
Monazite	$(Ce,La,Th,Y)PO_4$.
Rhabdophane	$(Ce,Y)PO_4 \cdot H_2O$.
Weinschenkite	$YPO_4 \cdot 2H_2O$.
Xenotime	YPO_4.
Multiple oxides containing columbium (niobium), tantalum, and titanium:	
Brannerite	$(U,Ca,Fe,Th,Y)_3Ti_5O_{16}$.
Eschynite-priorite series:	
Eschynite	$(Ce,Ca,Fe,Th)(Ti,Nb)_2O_6$.
Priorite	$(Y,Er,Ca,Fe,Th)(Ti,Nb)_2O_6$.
Euxenite-polycrase series:	
Euxenite	$(Y,Ca,Ce,U,Th)(Nb,Ta,Ti)_2O_6$.
Polycrase	$(Y,Ca,Ce,U,Th)(Ti,Nb,Ta)_2O_6$.
Fergusonite-formanite series:	
Fergusonite	$(Y,Er,U,Th)(Nb,Ta,Ti)O_4$.
Formanite	$(Y,Er,U,Tb)(Ta,Nb)O_4$.
Loparite	$(Ce,Na,Ca)(Ti,Nb)_2O_6$.
Perovskite [2]	$CaTiO_3$.
Pyrochlore-microlite series:	
Betafite	$(U,Ca)(Nb,Ta,Ti)_2O_7 \cdot nH_2O$.
Microlite [3]	$(Na,Ca)_2Ta_2O_6(O,OH,F)$.
Pyrochlore	$NaCaNb_2O_6F$.
Samarskite	$(Y,Er,Ce,U,Fe,Th)(Nb,Ta)_2O_6$.
Yttrotantalite	$(Fe,Y,U,Ca)(Ta,Nb,Zr,Sn)O_4$.

[1] May contain rare-earth elements.
[2] Cerian varieties known.
[3] Cerian and thorian varieties known.

monazite are in placers, but a few have been found in carbonatites and veins. Monazite, in addition to having been a major source of rare earths, has been the principal source of thorium. Its ThO_2 content is variable but is commonly in the 5–10 percent range. Although dominantly a mineral of the light rare earths, monazite generally has a higher content of yttrium and the heavy lanthanides than does bastnaesite.

Bastnaesite is a relatively rare mineral, and its use as an ore is largely the result of its concentrations in a very few large deposits, the most important of which is the carbonatite body at Mountain Pass, Calif. (Olson and others, 1954). Bastnaesite may also occur in veins, contact-metamorphic zones, and pegmatites, and as a rare accessory mineral in igneous rocks.

Xenotime, the yttrium phosphate, is found in the same environments as monazite, but is usually much less abundant.

Apatite, though not a rare-earth mineral, may incorporate these elements through substitution, commonly to the extent of less than half a percent of the total oxides but occasionally much higher. The light rare earths are usually dominant, although some apatites contain yttrium in excess of cerium (Cruft, 1966). The relationships between the rare-earth distribution in apatite and its geologic environment have been discussed by Fleischer and Altschuler (1969). Apatite is important as a potential source of rare earths, inasmuch as millions of tons of apatite-bearing rock are processed annually for the production of fertilizer materials.

A large proportion of rare-earth minerals is known only from minor occurrences, chiefly in pegmatites, but almost any one of these minerals may become important through the discovery of some new or long-unrecognized deposit.

TYPES OF DEPOSITS

Primary concentrations of rare-earth-bearing minerals are found in a wide variety of geologic environments, such as veins, gneisses and migmatites, skarns, pegmatites, and alkalic rock complexes and related carbonatites. Only a very few of these primary deposits have been mined successfully for rare earths alone. Notable exceptions are the vein deposits in Burundi in Central Africa, which produced more than 2,300 tons of bastnaesite between 1947 and 1956, and the bastnaesite deposit in carbonatite at Mountain Pass, Calif., which is probably the largest known rare-earth concentration. Some primary deposits have been exploited for other commodities, with rare earths as a byproduct. These include the monazite-apatite vein at Steenskampskraal in the Republic of South Africa (Pike, 1958), mined primarily for thorium, and apatite deposits in the U.S.S.R. and Finland, where rare earths are recovered from apatite processed for its phosphate content.

Unconsolidated secondary deposits—including sea-beach placers, river valley (fluviatile) placers, and deltaic deposits—represent by far the largest number of minable concentrations of rare-earth minerals and include many of the world's important sources. Monazite is the most common rare-earth mineral found in the placers, where it is invariably associated with other stable heavy minerals, such as zircon, garnet, magnetite, ilmenite, rutile, sphene, and xenotime. Sea-beach placers, notably those of Brazil and the west coast of India, have been the largest monazite producers. In the United States, fluviatile placers in the Southeastern States and in Idaho have been mined for monazite. A deltaic deposit at the mouth of the Nile has been worked sporadically. Some placers may be mined for monazite alone, but in many operations monazite is a byproduct or coproduct of placers that are worked primarily for zircon or for the titanium minerals ilmenite or rutile. Rare-earth minerals other than monazite generally are not recovered from placers. In the period 1956–59, however, the multiple-oxide mineral euxenite was mined, together with monazite and other heavy minerals, from fluviatile placers at Bear Valley, Idaho, primarily for niobium, but with an important amount of yttrium and heavy lanthanides as byproducts. Recovery of xenotime, an yttrium phosphate mineral, has recently been initiated as a byproduct of the tin placer mining in Malaysia.

Most consolidated sedimentary rocks have a very low rare-earth content, but with some important exceptions—phosphorites, fossil placers, and certain ancient conglomerates. The phosphorites, such as units in the Phosphoria Formation in the Western United States, represent vast resources of rare earths that are contained largely in apatite. Fossil placers—for example, those found in Upper Cretaceous sandstones in several Western States—commonly contain monazite, together with ilmenite, zircon, and other heavy minerals. The conglomerate type, as exemplified by the Huronian conglomerates of the Blind River area, Ontario, are mined extensively for uranium contained in the minerals brannerite and uraninite; monazite is also present in the ore. Recovery of yttrium oxide was begun in 1965 as a byproduct of uranium processing and continued as late as 1970. Although the ores have been esti-

mated to contain only 0.057 percent total rare-earth oxides (Jackson, 1968, p. 381), the production of yttrium oxide averaged more than 100,000 pounds per year during the 3-year period 1967–69.

RESOURCES

PRESENT SITUATION

The rare-earth industry in the United States is based largely on two main sources of raw materials—the bastnaesite deposit at Mountain Pass, Calif., and imported ores, chiefly monazite, from Australia and Malaysia. At times, these have been supplemented by unusual source materials, such as byproduct yttrium-rich residues from Idaho euxenite and Canadian uranium mills. Inasmuch as such sources have been ample to supply the 10,000 or so tons of rare-earth oxides now consumed annually in the United States, there is little incentive at present to search for and develop new deposits or to recover byproduct rare earths.

By the year 2000, the annual domestic requirements may be nearly 25,000 short tons for lanthanide oxides and about 180 short tons (compared with the present requirements of about 30 tons) for yttrium oxide, as estimated by Stamper and Chin (1970, p. 692, 801). The lanthanide requirements probably can be met easily from sources that are now being used, but the estimated sixfold increase in yttrium demand might necessitate its extraction from sources in the United States that have never been used. Reactivation of yttrium recovery from Blind River uranium mills can be anticipated, together with some increase over former production.

POTENTIAL RESOURCES

The foregoing discussion of types of rare-earth deposits will give some indication of the variety of environments in which the rare earths are likely to occur. Environments most favorable for the discovery of concentrations that could be mined solely for rare earths are very limited and are primarily carbonatites and placers. Concentrations in gneisses and migmatites so far discovered are currently of marginal value but may eventually become significant—particularly those containing xenotime, as at Music Valley, Calif. (Evans, 1964). When rare earths are considered as byproducts or coproducts, the field of potential producers is greatly expanded and will include many additional carbonatites and placers, both modern and fossil, thorite-bearing vein deposits, apatite-bearing magnetite deposits, and phosphatic rocks. Barite is a potential coproduct in some rare-earth deposits, such as those at Mountain Pass, Calif.

Many carbonatites and related rocks in alkalic complexes contain large tonnages of rare earths, not only in dominantly rare-earth species, as at Mountain Pass, but as proxying elements in other valuable minerals, such as the niobium ore pyrochlore and the phosphate ore apatite. In at least one foreign country, rare earths are currently being produced as a byproduct in the processing of apatite for fertilizer materials.

The apatite common in metasomatic magnetite deposits is generally high in rare earths, and such deposits are likely future sources of these elements, inasmuch as the apatite must be separated from the magnetite prior to smelting. Dumps at Mineville, N.Y., and Iron Mountain, Utah, contain large quantities of apatite; the Mineville apatite contains about 11 percent total rare earths (McKeown and Klemic, 1956, p. 6), and the apatite from Iron Mountain contains about 3 percent. Increases in the use of rare earths will make their recovery from this type of deposit feasible.

Another even larger untapped resource lies in the sedimentary phosphatic rocks, where the rare earths are also present in apatite. Such rocks are likely to be a much lower grade source of rare earths than apatite concentrates from carbonatites or iron deposits, but greatly exceed these in tonnage. Altschuler, Berman, and Cuttitta (1967) pointed out that in the national production of wet-process phosphoric acid in 1964, roughly 3,500 tons of elemental rare earths was made available by the solution of 6 million tons of apatite. This exceeded by more than 1,000 tons the domestic production of rare-earth oxides from bastnaesite and monazite ores during the same year. Altschuler's study of the feasibility of rare-earth extraction from phosphorites was based largely on phosphorite of the Bone Valley Formation in Florida, which has an elemental rare-earth content of about 0.06 percent. Higher rare-earth values were reported by Gulbrandsen (1966) for the phosphorites of the Phosphoria Formation in the Western United States; his average values for the Retort and Meade Peak Phosphatic Shale Members are 0.1 percent yttrium, 0.03 percent each for lanthanum and neodymium, and 0.001–0.003 percent ytterbium. Other rare earths were not included in the analyses. On the basis of these values, the 4 million or so tons of phosphate rock mined annually from the Retort and Meade Peak Members could contain as much as 4,000 tons of yttrium alone, more than 100 times the present demand. Reserves of phosphate rock in the United States are on the order of billions of tons. (See chapter entitled "Phosphate Deposits.") In the processing of phosphorites,

only about one-third of the tonnage used is put in solution by acids for manufacture of phosphoric acid, and this is the only part of the phosphate rock from which the rare earths are liberated; thus, any contemplated recovery would have to be made from this material.

Many current or potential sources of rare earths throughout the world are shown in table 117, to-

TABLE 117.—*Identified resources[1] of the rare earths and some potential rare-earth deposits of the world*

Country	Deposit	Type	Rare-earth oxides[2] (tons)	Remarks	References
Canada	Blind River-Elliott Lake	Conglomerate	1,200,000	Potential byproduct of U; some has been produced.	Shenk (1971); Griffith and Roscoe (1964).
	Oka	Carbonatite	Not evaluated	Potential byproduct of Nb.	Rowe (1958); U.S. Bur. Mines (1963).
	St. Honoré	----do	80,000	----do	Vallee and Dubuc (1970).
United States	Mountain Pass, Calif	----do	5,000,000	Reserve in bastnaesite ore.	Parker (1965).
	Music Valley, Calif	Metamorphic rocks	Not evaluated	Xenotime and monazite.	Evans (1964).
	Idaho-Montana placers, includes Bear Valley, Idaho.	Placers	147,600	Monazite and euxenite.	Eilertsen and Lamb (1956).
	Lemhi Pass, Idaho-Mont.	Thorite veins	84,000	Potential coproduct Th.	U.S. Atomic Energy Commission (1969); Staatz and others (1972).
	Mineral Hill district, Idaho-Mont.	Carbonatite veins	Not evaluated	Monazite, thorite, ancylite.	Anderson (1958).
	Bald Mountain, Wyo	Conglomerate	15,000	Monazite	Borrowman and Rosenbaum (1962).
	Wet Mountains, Colo	Thorite veins	1,750	Potential coproduct Th.	Christman and others (1959); Staatz and Conklin (1966).
	Powderhorn district, Colo.	Thorite veins and carbonatite.	4,000	----do	Olson and Wallace (1956); J. C. Olson (unpub. data).
	Gallinas Mountains, N. Mex.	Veins	Not evaluated	Bastnaesite with fluorite.	Perhac and Heinrich (1964).
	North and South Carolinas, and so forth (Piedmont area).	Stream placers, flood plains.	600,000	Monazite, minor xenotime in numerous scattered deposits.	Overstreet and others (1959).
	Hilton Head Island, S.C.	Beach placers	60,000	Monazite	McCauley (1960).
	Mineville, N.Y	Magnetite deposit	Not evaluated	Rare-earths in apatite, minor bastnaesite.	McKeown and Klemic (1956).
	Dover, N.J	----do	----do	Bastnaesite, doverite, xenotime.	Klemic and others (1962).
Brazil	Atlantic coast beaches and some inland areas.	Beach and fluviatile placers.	180,000	Monazite	Parker (1965).
	Morro do Ferro	Alkalic complex	300,000	Allanite, bastnaesite	Roser and others (1964).
	Araxá	Carbonatite	90,000	Potential byproduct Nb and apatite(?).	Do.
Uruguay	Atlantida	Beach placers	288	Monazite. Represents one sampled area.	Bogert (1959).
Bolivia	Llallagua area	Veins	Not evaluated	Monazite, minor xenotime in tin veins.	Gordon (1944).
U.S.S.R.	Kola area	Alkalic rocks and carbonatite.	6,800,000	Apatite, loparite. Tonnage based on potential byproduct from apatite processing.	British Sulphur Corporation, Ltd. (1971).
	Kyshtym area (Vishnevye Mountain).	Alkalic rocks, placers.	Not reported	Apatite, cerite, bastnaesite, allanite. Apatite contains 0.29–3.3 percent rare earths.	Zil'bermints (1929); Ganzeev and others (1966).
Nigeria	Plateau Province	Placers	----do	Small production from tin placers.	Mackay and others (1949).
U.A.R. (Egypt)	Nile delta	Fluviatile placers	120,000	Monazite. Intermittent production.	Higazy and Naguib (1958).
Burundi	Karonge mine	Veins	Not reported	Bastnaesite. Intermittent production.	Thoreau and others (1958).
Malawi	Kangankunde Hill	Carbonatite and residual soils.	68,000	Monazite	Deans (1966).
Kenya	Mrima (Jombo)	Alkalic complex and carbonatite.	300,000	Monazite; pyrochlore	Do.
Tanzania	Panda Hill (Mbeya)	Carbonatite	Not reported	Potential byproduct Nb and apatite.	Fawley and James (1955); Davidson (1956); Fick and Van der Heyde (1959).
Republic of South Africa.	Glenover	Carbonatite	----do	Synchisite, monazite	Verwoerd (1963).
	Steenskampskraal	Vein	9,000	Monazite. Has had large production.	Pike (1958); U.S. Bur. Mines (1964).
Zaire (formerly Republic of the Congo).	Shinkolobwe	----do	Not reported	Monazite	Derriks and Vaes (1956).
Malagasy Republic	Ft. Dauphin area	Placers	60,000	Monazite	Murdock (1963).
India	Chiefly in Kerala	Beach placers	3,000,000	Monazite	Wadia (1956).
	Bihar and west	Alluvial placers		----do	Parker (1965).
Ceylon	Chiefly west and northeast coasts.	Beach placers	6,000	Monazite. Tonnage given is from one northeast coast deposit.	Davidson (1956).

See footnotes at end of table.

TABLE 117.—*Identified resources[1] of the rare earths and some potential rare-earth deposits of the world*—Continued

Country	Deposit	Type	Rare-earth oxides[2] (tons)	Remarks	References
Malaysia	Various	Placers	Not reported	Monazite, xenotime. Byproduct of Sn.	Do.
Indonesia	----do	----do	----do	Monazite	Olson and Overstreet (1964).
Taiwan	Coastal areas	Beach placers	6,000	----do	Shen (1965).
Korea	Various	Stream and beach placers.	64,900	Monazite. Tonnage from evaluated deposits only.	Olson and Overstreet (1964).
Australia	----do	Beach placers	480,000	Monazite	Parker (1965).
	Mary Kathleen	Contact metamorphic	Not reported	Allanite, stillwellite in U deposit.	Matheson and Searl (1956).
	Radium Hill	Veins	----do	Brannerite	Barrie (1965).
Total (rounded).			18,666,000		

[1] Identified resources: Specific, identified mineral deposits that may or may not be evaluated as to extent and grade, and whose contained minerals may or may not be profitably recoverable with existing technology and economic conditions.
[2] Monazite assumed to contain 60 percent and euxenite 15 percent rare-earth oxides.

gether with data on their reserves or resources, where such information is available. For some deposits the rare-earth tonnage has been derived indirectly from data in the cited references. The total resource potential, more than 18½ million tons, does not include the resources of rare earths in the sedimentary phosphatic rocks but does include the igneous apatite of the Kola Peninsula.

Only a fraction of this rare-earth potential can likely be recovered. Some deposits, such as many of the monazite placers in the Southeastern United States, either are too small to be worked or are on land too valuable for other purposes to be mined. Where rare earths are a potential byproduct, as in deposits mined for uranium, niobium, or phosphate, there will be no recovery without sufficient demand.

PROSPECTING TECHNIQUES

The discovery of rare-earth deposits is likely to be an accidental adjunct to the search for radioactive materials. This was true of the Mountain Pass bastnaesite deposit, where a local radioactivity anomaly due to thorite attracted the attention of prospectors. Numerous other rare-earth occurrences, for the most part uneconomic, were found during the period when the use of portable radiation-detecting instruments became commonplace. Many of these discoveries were made because of the radioactivity of monazite, which normally contains several percent thorium. Bastnaesite, however, is not itself appreciably radioactive, and where it is largely unaccompanied by thorium or uranium minerals, as in the Gallinas Mountains, N. Mex. (Perhac and Heinrich, 1964), radioactivity is of little value in prospecting.

Lanthanide ions—notably those of neodymium, praseodymium, erbium, and holmium—produce absorption bands in the spectrum of light transmitted by many of the minerals in which they are present. These bands are easily seen with a hand spectroscope or microspectroscope when the mineral is illuminated by a strong source of white light (Adams, 1965). Samples can be examined in the field using sunlight, but they can be examined more effectively in the laboratory. The mineral grains must be sufficiently translucent to transmit some light, as is commonly true of bastnaesite, monazite, and xenotime. The use of this technique in the examination of panned concentrates was suggested by Mertie (1954).

The recognition of cerium subgroup minerals by the use of unfiltered light from an ultraviolet lamp has been described by Murata and Bastron (1956). The emerald green shown by the minerals is due to the absorption of certain wavelengths of light by neodymium and praseodymium and is a very useful preliminary test for bastnaesite, monazite, and some other nonopaque rare-earth minerals.

Many rare-earth-bearings materials are not recognizable by mineralogical examination, particularly when these elements are present in carrier minerals such as apatite, sphene, zircon, or thorite. For such rocks some analytical method such as X-ray fluorescence or emission spectrography (Parker and Baroch, 1971) must be used.

PROBLEMS FOR RESEARCH

Although known resources of rare earths are large, they undoubtedly can be increased by continued investigation of geologic materials in all parts of the world. Some potential domestic sources are not evaluated, and many others remain to be discovered. Resources in the apatite of phosphorites and iron deposits are impressive but are of little value until economic methods of recovery are developed, and research in this field is needed in anticipation of their eventual use. This is also true for the resources in thorite veins, where the rare earths may be an important coproduct. (See "Thorium" in chapter on "Nuclear fuels.")

A major problem in the rare-earth field, however, is not one of scarcity of raw materials, but rather of developing a better balance in the utilization of all the rare-earth elements normally recoverable from the ores. The ore minerals bastnaesite and monazite contain the individual rare earths in characteristic, though somewhat variable, proportions, with cerium subgroup elements predominant. Thus, a ton of bastnaesite may contain about 700 pounds of cerium oxide but only 1½ pounds of europium oxide. These relationships, which are established by the natural distribution of the elements in the ores, cause no problems when the demand for mixed or separated elements is roughly proportional to their abundance. If, however, an unusual demand arises for one specific element, as for europium, its extraction can result in the unavoidable production of other lanthanides in excess of existing requirements. Increased uses for the more abundant rare earths and significant uses for some of the scarce ones would be of great value in stabilizing the industry, and it is in the discovery of these uses that further research is needed.

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RHENIUM

By R. U. King

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ABSTRACT OF CONCLUSIONS

Rhenium, a rare element that has only recently come into significant industrial use, has properties excellently suited for application as a refractory metal, as an alloying element, in high-temperature thermocouples, in electronic components, and as a catalyst in petroleum refining. Rhenium is obtained from molybdenite that is recovered as a byproduct of copper production, and the supply of rhenium, as well as the world resources of rhenium is therefore closely tied in with the world's resources of molybdenum in porphyry copper deposits.

Identified U.S. resources of rhenium are estimated to be about 10,000 short tons, and world resources on the order of 30,000 short tons. Although other sources may exist, they are not known to be significant.

INTRODUCTION

Rhenium, one of the rarest and most dispersed of the metallic elements, has been intensively studied since its discovery in 1925. Rhenium metal is silvery gray and has a melting point of about 3,180°C, the second highest of all metals (after tungsten). It has a density of 21 grams per cubic centimeter, the fourth heaviest of the metals; it is almost as heavy as platinum. It is ductile, extremely hard, and high in tensile strength. Wrought rhenium metal resists oxidation, but rhenium in powder form oxidizes readily at the moderate temperature of 150°C. Rhenium does not occur in its native or pure state but only in combination with other elements, and no definite rhenium minerals have yet been identified. It has been found in significant concentrations only in association with molybdenite.

Rhenium, atomic number 75, is a heavy transition metal that can form an extensive series of compounds that include the widest range of valences of any element, from —1 to +7. Rhenium is placed in column 7B of the periodic table, below manganese and technetium, adjacent to tungsten and the platinum metals, and diagonally below molybdenum. It has a marked affinity for sulfur, as does molybdenum. The association with molybdenum is marked, but there is evidence of only a slight association with manganese, the platinum metals, and tungsten (Fleischer, 1959). Unique features of rhenium chemistry are the unusually high volatility of the heptoxide and the high solubility of the heptoxide in water and oxygenated solvents.

Various figures are given in the literature for the abundance of rhenium in the earth's crust, ranging from 0.5 to 10 parts per billion.

USES

The principal uses of rhenium are as an alloying element in specialty metals, in high-temperature thermocouples, in filaments of mass spectrographs and ion gages, in electronic and electrical control devices, flash lamp filaments, metallic coatings, heat-, wear-, and corrosion-resistant alloys, and as a catalyst in petroleum refining to produce high-octane gasoline (Shimamoto, 1972). Its high melting point and module of elasticity and its heat-stable crystalline structure make rhenium an excellent refractory metal.

In view of the current attention being placed upon environmental pollution, particularly as related to modern gasoline-powered transportation, the beneficial properties of rhenium as a catalyst in the petroleum-refining industry may make it of great national importance in the very near future. High-octane gasoline is produced more economically

by the use of bimetallic catalysts, such as platinum-rhenium. Rhenium does not substitute for platinum in the refining (rheniforming) process, but acts as a promoter for the platinum catalyst.

EXPLOITATION

Rhenium is produced only in connection with the industrial practice of roasting of molybdenite concentrates that contain about 100 to 2,000 ppm (parts per million) rhenium (Churchward and Rosenbaum, 1963). Such concentrates are almost exclusively those that are prepared as a byproduct from the mining of the porphyry copper-molybdenum ores of British Columbia, Western United States, Mexico, Peru, Chile, and Russia.

In the United States, current production of rhenium, totaling only a few tons per year, comes from its recovery from flue dusts that accumulate during the conversion of byproduct molybdenite concentrates to molybdenum trioxide.

Current technology permits recovery of rhenium from those deposits in which the rhenium content of the molybdenite is at least 100 ppm.

Earliest recorded commercial production of rhenium was in 1930 when small amounts of the metal were recovered from copper smelter wastes at Mansfeld, Germany.

In the U.S. rhenium production began in 1942 at the University of Tennessee, with the recovery there of a few hundred pounds from smelter flue ducts from the Miami Cooper Co.'s plant in Arizona; sizable production did not begin until 1954 when the Kennecott Copper Corp. began to recover rhenium from some of the copper-molybdenum ores. Annual production of rhenium increased markedly during the early 1960's from about 1,000 pounds in 1962 to about 4,000 pounds in 1966, according to annual reports of the U.S. Bureau of Mines.

In 1960 the world's recoverable reserves of rhenium were estimated to be greater than 500 tons, U.S. reserves amounting to about 65 percent of the total. World production in 1965 was about 5,000 pounds of rhenium. The price of rhenium has ranged widely over the years, from $400 to $800 a pound.

RESOURCES

The principal rhenium resources consist of trace amounts occurring in the molybdenite that accompanies the copper ores of porphyry copper deposits. Rhenium is also present in the molybdenite of the porphyry molybdenum deposits, in contact-metamorphic tungsten-molybdenum deposits, molybdenum-bearing pegmatites, and molybdenite-bearing quartz veins. It also occurs with molybdenum and uranium in bedded deposits in sandstone, in bituminous copper-bearing shales, in vanadiferous black shales, and in cupriferous sandstone deposits.

The molybdenites of porphyry copper deposits contain from about 100 to 3,000 ppm rhenium, several times that in other types of deposits. Although notable exceptions are known, in which rhenium concentrations exceed 2,000 ppm, these exceptions represent deposits containing tonnages too small to be of economic significance under present conditions (Peterson and others, 1959).

Identified resources of rhenium in porphyry copper deposits are estimated to be about 10,000 short tons in the United States and on the order of 30,000 short tons in the entire world. These estimates are calculated from the identified resources of molybdenite in porphyry copper deposits as detailed in "Molybdenum" of this volume, assuming an average rhenium content of 800 ppm in the molybdenite (=1,333 ppm Re in Mo) of such deposits.

Because the only known readily available source of rhenium is molybdenite, speculation as to additional resources must be related to molybdenum resources. Nongeological factors, however, may operate independently of the relation of rhenium to molybdenum, to add significantly to the rhenium resource base. Such factors include potential improvement in the technology of recovery, which may make it possible to profitably recover rhenium from the very large resources of molybdenite in the molybdenum porphyry deposits; improvements in process metallurgy; and discoveries of new uses, which may reduce costs of end products, with resulting increase in demand for rhenium and possible increase in its price. Owing to these factors and to the variability of the rhenium content in molybdenite, any attempt at present to quantify the hypothetical and speculative resources of rhenium would have very little meaning.

PROBLEMS FOR RESEARCH

Considerable variation in rhenium content of molybdenite from different parts of a deposit has recently been noted. Determining average values for rhenium in molybdenite in large deposits requires analysis of many samples, still a time-consuming and expensive process; the only alternative today is to depend on analyses of mill concentrates for these average values. Further research into analytical techniques seems warranted in order to permit adequate sampling of the large low-grade porphyry deposits, to delineate variations of rhenium in molybdenite, and to obtain better under-

standing of zonal distribution of rhenium in copper-molybdenum deposits.

Rhenium minerals have not yet been isolated, with the possible exception of a rhenium copper sulfide from Russian deposits; moreover, the structural relation of rhenium in molybdenite is not well understood. Research into these aspects of rhenium mineralogy seems warranted.

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SAND AND GRAVEL

By Warren Yeend

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ABSTRACT OF CONCLUSIONS

The sand and gravel industry is the largest nonfuel mineral industry in terms of volume, in the United States. Although the United States currently produces enough sand and gravel to supply its requirements, it is predicted that by A.D. 2000 the domestic resources accessible at 1968 prices will barely meet the demand.

The most important commercial sources of sand and gravel are river channels and glaciated terrain. However, as these sources become depleted, marine and lake environments could become important.

Deposits in all areas are located by conventional field mapping with the aid of geophysical techniques, such as seismic refraction and reflection and resistivity surveys.

A current major problem facing industry is land-use conflict where land containing potentially rich sand and gravel resources is at present more valuable for building development and is thus removed from future mineral production. Planning resulting in effective multiple use of the mineral-rich land would allow for the recovery of sand and gravel prior to urbanization.

Additional sand and gravel now noneconomic may be made available through development of low-cost transportation from remote deposits or by the establishment of a workable two-way (back haul) exchange system.

INTRODUCTION

The sand and gravel industry is the largest nonfuel mineral industry, in terms of volume, in the United States. Although this commodity possesses the lowest average unit value of all the mineral commodities ($1.11 per ton in 1968), its total production value in 1970 was approximately $1.1 billion, surpassed by only a few mineral commodities.

The construction industry accounts for 96 percent of all domestic consumption of sand and gravel, the principal uses being concrete aggregate, bituminous mixes, and fill.

At present the United States is entirely self-sufficient and produces enough sand and gravel to supply all domestic requirements. However, because of the continual increasing cost of land, equipment, and personnel, as well as widespread zoning and environmental limitations, the outlook for the industry is uncertain and not without problems. Domestic resources now accessible at 1968 prices are barely adequate to meet the maximum cumulative forecast demand of 66 billion tons by the year 2000 (Cooper, 1970). Transportation costs severely limit international trade in sand and gravel; thus, it is not surprising that less than 1 percent of the sand and gravel used in the United States is imported.

Domestic production of sand and gravel in 1970 was 943.9 million short tons, 43 percent of which was produced in seven States—California, Michigan, Ohio, Minnesota, Illinois, Wisconsin, and New York. Of the 100 largest sand and gravel operations in the United States, almost all are near the large population centers. The San Francisco Bay and Los Angeles areas account for 27 of the 100 largest operations. Most of the remainder are east of the Mississippi River in the Northern States, where the bulk of the population of the country is centered. Fortunately, much of this area falls within the glaciated area of the United States, which is a rich source area for sand and gravel deposits.

Although there seems to be an increasing need, the demand for this commodity has, in the past, fluctuated locally as a function of construction of large public works projects, such as dams, freeways, and aqueducts. Such construction consumes by far the greatest tonnages of sand and gravel. A prediction of future need, therefore, hinges on a pre-

diction of future public-works projects. As the Nation becomes urbanized with a high population density, the need for more public-financed dams and highway projects may decrease. New forms of mass transit and housing structures, however, will place increased demands on the sand and gravel industry.

GEOLOGIC ENVIRONMENTS AND THEIR DISTRIBUTION

Sand and gravel are unconsolidated rocks and minerals ranging in size from silt (0.0039 mm) to boulders, formed by the breakdown, erosion, and transport of bedrock by ice, water, and wind. The precise definition and specifications for sand and gravel are extremely variable and commonly so complex that generalization is difficult. However, gravel generally has an upper size limit of 3½ inches in diameter and a lower limit of one-fourth of an inch, and sand particles are 1/4–1/16 of an inch in diameter (Industrial classification of the American Society for Testing and Materials).

Ideally, a commercial deposit contains 60 percent gravel and 40 percent sand (Goldman, 1961). This provides ample coarse material to crush for road base or bituminous aggregate, and sand in the correct sizes and proportions for use in concrete. In addition, the aggregate used for concrete should be essentially free of clay, silt, mica, organic matter, chemical salts, and surface coatings.

The primary commercial sources of sand and gravel are along existing or ancient river channels and in glaciated terranes; marine and lake environments have been less important source areas. Water is the sculpturing, sorting, cleansing, and transporting agent that is responsible for the flood-plain, outwash-plain, stream-terrace, alluvial-fan, esker, kame, delta, and moraine deposits that form the principal commercial deposits of sand and gravel. Windblown deposits locally are of minor economic importance.

The sand- and gravel-rich geologic environments differ throughout the United States. The distribution of the most abundant deposit types on a countrywide geographic basis is as follows: Northern States, glacial outwash and till; Atlantic and Gulf Coast States, marine terraces; Southeastern and South Central States, river deposits; Mountain States, stream and fan deposits; Great Plains, stream deposits; and Pacific Coast States, alluvial fans, river deposits, river terraces, beaches, and dunes.

California leads all other States in sand and gravel production, of which 75 percent of the sand and gravel is produced from stream deposits. The huge alluvial-fan deposits in both the San Francisco and Los Angeles areas are the main sources of sand and gravel, but stream-channel deposits are also widely exploited. The stream deposits throughout the State are important sources for sand and gravel primarily because of their widespread availability, but other factors, such as thin overburden, nearness to water necessary for processing, and yearly replenishment by spring flooding, are important. The average particle size changes along a river channel, generally providing a variety of differently sized material for specific needs. The natural abrasive action prevalent during stream transport removes the nonresistant particles and concentrates the durable ones. Stream-produced subrounded to well-rounded particles are particularly desirable for use in concrete.

Glaciofluvial deposits, eskers, kames, and outwash provide the bulk of the sand and gravel in the Midwestern and Northeastern States. These deposits are favorable sources for sand and gravel because they are common and widespread, possess little deleterious material, and are generally free of overburden.

In 1964 only 3 percent of the United States production of sand and gravel (including shell deposits) came from the ocean floor (Emery, 1966). As land sources are exhausted or removed from production for various reasons, the offshore deposits will probably be more extensively exploited.

Bedded pre-Quaternary semiconsolidated sandstones and conglomerates deposited in ancient alluvial, lake, or marine environments have rarely been used as sources for sand and gravel. This type of deposit, while having a potential advantage of almost unlimited tonnages, has such disadvantages as thick overburden, high content of weathered, friable particles, high percentage of clay, and enough induration to require crushing. The use of such deposits is currently limited, although the Pliocene Kern River Formation in southern California has been utilized as a sand and gravel source (Goldman and Klein, 1961).

POTENTIAL RESOURCES

The estimated potential resource of sand and gravel in the United States is of little value unless costs of production are considered. A bulk tonnage not only would be difficult to estimate, but also would be meaningless without an economic frame of reference. Considerations, such as location, tonnage, quality, accessibility, and economic availability to markets, must be included in meaningful evaluations. In the near future shortages of sand

and gravel will result from uneven distribution of deposits, depletion of local deposits, urban encroachment, increased cost of property acquisition, and higher transportation costs (Sheridan, 1967).

Goldman (1966, p. 369), an authority on sand and gravel in California, stated that "there are no undiscovered deposits near the metropolitan areas that can be developed to meet demand * * *. The State faces depletion of its major sources within the next 3 decades unless sand and gravel deposits can be set aside as natural resource zones for future use." Thus, it may become necessary to import sand and gravel from beyond the present economic limit of 50 miles. Consequently, we are faced with the task of correctly and effectively utilizing the known deposits. This will, in large part, be controlled by the zoning and planning officials of city governments. The geologist's role, therefore, may be merely to draw attention to the limits of the deposits and to point out that these deposits are the total resource existing within the economic radius of the population center.

Crushed rock materials other than the conventional unconsolidated river and glacial deposits are potential sources that should be considered; however, they have been neglected for specific reasons. Hard-rock mine dumps are potential resources of aggregate; however, although such material has had some use as road base, it is generally unsuitable for concrete aggregate because it lacks proper size and gradation and contains harmful sulfide minerals (Goldman, 1956). Artificially crushed stone is also useful for road base where angular shape is desirable, but when crushed stone is used in concrete, more cement is required, and more care is necessary in mixing and pouring than with conventional gravel. In the Tucson, Ariz., area, however, it has been forecast that "probably within 10 years coarse aggregate will be supplemented by broken and crushed rock quarried from nearby mountains" (Williams 1967).

Dredge tailings generally consist of coarse gravel overlying fine-grained material, from which it is costly to obtain a "good blend"; however, many of these deposits are an excellent source of coarse aggregate.

Pre-Quaternary rocks may be potentially useful but are generally too firmly cemented or contain too much weathered clayey material (Goldman, 1956).

Marine and lake environments may offer some of the best potential source areas. Such environments should be target areas in a search for large blanket-type aggregate deposits. Much of the continental shelf from New England to New Jersey is mantled by sand associated with lesser amounts of gravel "* * * in a quantity probably sufficient to constitute an economic asset" (Schlee, 1968). As the population continues to increase along the east coast (Washington, D.C.–Boston), demand for offshore supplies of sand and gravel will markedly increase (Emery, 1966).

The underwater Great Lakes sand and gravel deposits continue to grow in importance as upland sources diminish by depletion, zoning, and high transportation costs. Large quantities of high-grade aggregate are already being extracted in western Lake Erie and along the Lake Ontario and Erie shorelines (Woodrow and others, 1971).

EXPLORATION TECHNIQUES

Surface geologic mapping is perhaps the simplest and most common method by which sand and gravel deposits are located. Data are gathered by geological examination of streambanks, roadcuts, excavations for building foundations, and any other natural or manmade exposure of surficial material. With the aid of aerial photographs and topographic maps, and a knowledge of the types of landforms commonly underlain by sand and gravel, the geologist can pinpoint potential resource areas for detailed field examinations. After a deposit is located, the geologist must determine thickness, lateral extent, possible tonnage, and overburden depth, and he must collect representative samples for specific determinations. Records of drill holes from oil, gas, or water wells can be used when available to give valuable information in the subsurface dimension, particularly pertaining to the thickness of sand and gravel deposits.

In the absence of drilling data, information about the depth and lateral extent of sand and gravel can be obtained with the aid of several different geophysical tools. Seismic refraction is a particularly sensitive method for determining depths and thickness of sand and gravel in certain geologic situations (Peterson and others, 1968). This method works best where less dense materials (sand and gravel) overlie denser materials (bedrock or fill). If a very dense overburden overlies an aggregate source, the presence of the aggregate is not likely to be determined by use of the seismic method because the shock waves will be diffused downward into less dense material. In areas of shallow bedrock, shallow seismic devices employing a sledge hammer or firecrackers rather than a dynamite charge can be used (Criner, 1966).

Another geophysical method used to determine thickness of sand and gravel is electrical resistivity.

The method is generally used to measure texture; thus, bedrock would normally have a high resistivity compared with overlying unconsolidated materials. By using different electrode spacings, it is possible to "probe" to various depths and obtain a general idea of depths and thickness of layered units overlying bedrock. The method has been used successfully in a wide range of geologic environments and is a much cheaper way to obtain subsurface information than drilling (Bruce and Lundberg, 1964; Peterson and others, 1968).

Surface samples and bottom photographs provide the best data for locating sand and gravel in offshore marine environments, although vibrocoring or drilling supplemented by seismic-reflection profiles are needed for determination of thickness (Emery, 1966). Seismic profiles across the continental shelf on the east coast show that a fairly uniform covering of sand and some gravel a few meters thick is present on the ocean floor (Schlee, 1968).

PROBLEMS FOR RESEARCH

The sand and gravel industry, like many of the mineral industries, is currently beset with a wide variety of source and utilization problems. The major problem centers on land-use conflicts where land containing potentially rich sand and gravel resources is found to be more valuable for other uses and is removed from mineral production.

A great deal more sand and gravel is being covered by manmade structures than is being produced for consumption (Cooper, 1970). A report on the Denver, Colo., area disclosed that four times as much aggregate has been lost through expansion of the city and suburbs into areas containing potential usable sand and gravel deposits than had been consumed in construction (Sheridan, 1967). The situation is probably similar in many other metropolitan areas in the United States. The millions of cubic yards of sand and gravel lost annually could be made available with better planning. Areas adjacent to large population centers should receive high priority in locating and preserving future sand and gravel resources.

The heavily populated and urbanized Middle Atlantic, New England, and Pacific Coast States present the most immediate problems with respect to sand and gravel resources because of (1) the rapid depletion of currently operated deposits, (2) the covering of potential resources by urban structures, and (3) opposition to environmental disturbance that might result from sand and gravel operations.

If we are going to have sand and gravel for use, more efficient multiple use of the land will be required. Numerous examples of beneficial multiple land use are demonstrated in the metropolitan Denver, Colo., area (Sheridan, 1967). Initially, the sand- and gravel-rich lands were used for agriculture. Later, sand and gravel were extracted, and the mined-out areas were subsequently used or are now serving as critically needed sanitary land-fill sites (garbage dumps). When the land is restored to a usable profile and grade, it is reclaimed in one of many ways, such as building sites for industrial and commercial structures, shopping centers, or churches, or as sites for recreational facilities, streets, freeways, or parking lots. "The conversion has been so complete and successful that, at many locations, nothing remains to indicate that the relatively temporary extractive operation existed" (Sheridan, 1967). More of these successful multiple-land-use projects are needed as vast acreages of sand and gravel have been lost to production by the rapid urban sprawl. Equally large deposits remain, however, in urban areas from which, with thoughtful planning, the mineral potential can be realized while still preserving the land for later use. Several fairly detailed studies of site utilization and rehabilitation practices for sand and gravel operations have been made (Schellie and Rogier, 1963; Johnson, 1966; Bauer, 1965; Ahearn, 1964). The widespread implementation of these practices is needed.

Environmental limitations are factors that must be considered in the location and development of sand and gravel deposits. The effects of traffic, smoke, dust, noise, vibration, perils of excavation or ponds, hazards of mining equipment, depression of property values, unsightliness, water pollution, and lowering water table must be determined prior to the mining.

The threat to animal and plant life, streambed and runoff changes, and local flooding are problems associated with the dredging of sand and gravel that put limits on the location and type of deposits which can be used.

Large quantities of water are needed for processing most sand and gravel deposits, and the availability of abundant, cheap water is becoming a factor in the location of plants.

Local problems of the sand and gravel industry vary in different geographic areas. In the Tucson, Ariz., area, for example, problems are principally those of (1) the thinness (8–10 ft) of the gravel beds, (2) presence of caliche, which cements the gravel and is a deleterious material, (3) inadequate supplies of water, (4) thick overburden, and (5)

hot weather causing rapid setting of cement, thus requiring a short haul limitation for mixed cement (Williams, 1967).

Many of the major problems associated with the industry could be eliminated if a cheap means of transporting sand and gravel were available. Transportation costs of this large-volume, low-unit-value commodity limit the distance the deposit can be from the market and still be economical. In California, this distance is roughly 40 to 50 miles (Goldman, 1968), and in Oregon, less than 20 miles (Schlicker, 1969). In some areas where the "back haul" can be utilized for some other commodity, the distance increases, as in the Denver area, where sand and gravel are back-hauled as much as 160 miles east of the city by Kansas grain trucks (Sheridan, 1967).

Perhaps the key to the future of the industry is to develop a cheap form of transportation to and from the metropolitan centers. What do the people in the metropolitan areas have in excess that they would like to get rid of in exchange for sand and gravel? Garbage! Perhaps unit trains could be used to exchange garbage for sand and gravel in sparsely populated areas. The garbage could be used as backfill, thus producing little noticeable change on the shape of the landscape.

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SCANDIUM

By John W. Adams

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ABSTRACT OF CONCLUSIONS

Scandium is a rare metal that at present has only minor industrial applications. Geochemically, it is a highly dispersed element that occurs chiefly in trace amounts in the ferromagnesian minerals of igneous rocks. Scandium may be concentrated in pegmatites, some of which have been mined for thortveitite, one of the few independent scandium minerals. It may also be present in anomalously high amounts in some phosphate deposits and tungsten ores. Some scandium has been produced from domestic and foreign uranium ores in mills where it accumulated in residues that developed during the extraction of uranium. Scandium apparently is not being recovered from any source at the present time, but if demand were to increase, the element could be obtained again as a byproduct of uranium-ore processing as well as from certain tungsten ores and phosphatic rocks.

INTRODUCTION

Scandium (Sc) is a soft silvery metal that was discovered in 1879 but was not prepared in its metallic form until 1937. It has atomic number 21 and is trivalent. It is sometimes included as a member of the rare-earth group but differs markedly from the rare earths in its geochemical behavior.

Scandium is a commodity whose statistics of production and demand are quoted in grams rather than tons. Until a few years ago, its sole and very limited commercial use was as a tracer of fluid flow in oil wells. This purpose requires the irradiation of natural Sc^{45} in a nuclear reactor to produce the radioactive isotope Sc^{46}, which has a half life of 84 days. Recently, however, a new application for scandium has been found in high-intensity lamps—the metal produces light in a more balanced color range. Several thousand grams of scandium are now used in these lamps annually (U.S. Bur. Mines, 1971).

Scandium is an expensive metal owing to both the cost of extraction and the very limited demand. In the past, it has been obtained almost exclusively from the rare mineral thortveitite, a scandium-yttrium silicate mined in Norway and Madagascar, but since 1960 its chief source has been waste products from certain uranium mills that use an organophosphate solvent extraction process for uranium recovery (Ross and Rosenbaum, 1962). Scandium has not been produced from uranium mills in the United States for several years, and the limited demand has been met from producers' stockpiles or from imports from Canada and Australia (U.S. Bur. Mines, 1971).

Should the need for scandium increase drastically, it could be produced from several possible sources, but its price would probably always be high if low-grade raw materials had to be used.

GEOLOGIC ENVIRONMENT

GEOCHEMISTRY

Scandium tends to be dispersed like the rare-earth elements, but it is dispersed to an even greater degree. Its crustal abundance has been variously estimated to be 5–30 ppm (parts per million) (Fryklund and Fleischer, 1963; Parker, 1967), about that of some lanthanide elements, but much greater than that of such familiar elements as antimony, mercury, molybdenum, and silver, which are more readily available owing to their tendency to

accumulate in enormously high concentrations in localized sites.

Most of the scandium in the earth's crust is contained in igneous rocks, where it is largely a trace constituent of the ferromagnesian minerals. These minerals may commonly contain 5–100 ppm Sc_2O_3 (Frondel, 1968, p. 122). Pyroxenes, hornblende, and biotite are the usual hosts for scandium; therefore, rocks rich in these minerals, notably the mafic rocks, will have the highest scandium contents. Analyses of 76 samples of igneous and sedimentary rocks, including nine composite samples, reported by Norman and Haskin (1968), showed that the highest scandium contents (30–40 ppm) are in basalts and gabbros and the lowest (about 1 ppm) in nepheline syenites and limestones.

Scandium in the ferromagnesian minerals apparently substitutes for iron in sites occupied by either (Fe^{+3},Al) or (Fe^{+2},Mg). Scandium can also form limited solid solution with Y^{+3}, Al, the heavy lanthanides Er^{+3} to Yb^{+3}, Ti^{+4}, Sn^{+4}, Zr^{+4}, and W^{+6} in certain geochemical environments. Where scandium is substituting for higher valence ions, such as Ti^{+4} or W^{+6}, a complex coupling mechanism involving $(Nb,Ta)^{+5}$ and Fe^{+3} may be required for charge balances in some minerals (Frondel, 1968).

MINERALOGY

Scandium is an essential constituent of very few minerals and these are all very rare species. These minerals are:

Thortveitite	$(Sc,Y)Si_2O_7$
Sterrettite (Kolbeckite)	$Sc(PO_4)2H_2O$
Bazzite	$Be_3(Sc,Al)_2Si_6O_{18}$
Magbasite	$KBa(Al,Sc)(Mg,Fe)_6Si_6O_{20}F_2$

Many additional minerals may contain scandium in amounts that range from a few to thousands parts per million through substitution by one or more of the mechanisms mentioned above. In addition to being found in the ferromagnesian minerals, scandium is found in multiple-oxide minerals of the rare earths, columbite, wolframite, cassiterite, beryl, garnet, muscovite, and aluminum phosphate minerals. The scandium contents of these and many other minerals have been reported by Neumann (1961), Borisenko (1963), Vlasov (1964), Phan, Foissey, Kerjean, Moatti, and Schieltz (1967), Frondel, Ito, and Montgomery (1968), and Frondel (1970a,b). Inasmuch as several of the minerals that are scandium carriers are also important ores of other elements, byproduct recovery is a distinct possibility.

TYPES OF DEPOSITS

PEGMATITES

Granitic pegmatites have so far been the only source of the high-grade scandium ore mineral thortveitite. Thortveitite-bearing pegmatites, known from only a few places in the world, have been mined for scandium in the Iveland-Evje district in Norway and in Madagascar.

In Norway, at least 10 pegmatites have produced thortveitite, but the aggregate recovery by 1961 was only about 50,000 grams (Neumann, 1961). The Befanomo pegmatite in Madagascar, apparently exhausted by 1955, supplied 38,000 grams (Murdock, 1963, p. 101).

Neumann's (1961) study of the Norwegian pegmatites shows that most of the scandium is contained in iron minerals, chiefly biotite and ilmenite, and that minerals from dikes in which thortveitite is present are richer in scandium than those from dikes without thortveitite. Neumann suggested that a deficiency of divalent iron, for which scandium commonly proxies, would favor the development of thortveitite in a pegmatite.

Quite similar observations were made by Phan, Foissy, Kerjean, Moatti, and Schieltz (1967) from their work on Madagascar pegmatites. They noted that one rarely finds a rich scandium mineral if the associated minerals are scandium poor and that one can observe in the majority of mineral deposits the following decreasing order of tenor: Thortveitite, niobium-tantalum minerals (metamict minerals, columbite-tantalite, ilmenorutile), muscovite, garnet, beryl, and tourmaline.

The only known occurrence of thortveitite in the United States is in the Crystal Mountain fluorite deposit in Montana (Parker and Havens, 1963). This deposit, described by Taber (1952, 1953) and by Weis, Armstrong, and Rosenblum (1958), consists of tabular bodies of fluorite in coarse-grained biotite granite that contains xenoliths of biotite-quartz-plagioclase gneiss, hornblende-plagioclase gneiss, and pegmatitic granite. Gangue minerals in the fluorspar are altered feldspar, sericite, quartz, and biotite. Massive quartz overlies the west outcrop (Geach, 1963). Radioactive zones, such as described by Weis, Armstrong, and Rosenblum (1958, p. 20), lie along the margins of the fluorite bodies. These zones consist largely of dark-purple fluorite and contain considerable biotite. Accessory minerals include sphene, quartz, oligoclase, apatite, green amphibole, fergusonite, thorianite(?), and thortveitite (Parker and Havens, 1963).

Limited geologic information on the Crystal Mountain deposit suggests a magmatic origin. One

might speculate further that the pegmatite is actually unusual. If it is unusual, the massive quartz body mentioned by Geach (1963) would be an asymmetric core, the fluorite bodies an intermediate zone, and the radioactive layers the wall zone.

The Crystal Mountain deposit has been actively mined for fluorspar since 1952, but there is no indication that thortveitite or other minerals have been recovered.

The influence of host rock on the scandium content of pegmatites has been long considered and is discussed by Neumann (1961) and Phan, Foissy, Kerjean, Moatti, and Schieltz (1967). Amphibole-bearing rocks seem definitely favorable for scandium pegmatites, but an amphibolite host rock is no assurance that a pegmatite will be enriched in scandium.

GREISEN AND VEIN DEPOSITS

Metasomatic deposits containing minerals of tungsten, tin, or beryllium in association with quartz, muscovite, topaz, or tourmaline are found in or near granitic bodies from which they, and related high-temperature veins, presumably were derived. These deposits, called greisens, are apt to contain minerals with anomalously high scandium content. According to Borisenko (1963), the main scandium carriers in greisens are wolframite, cassiterite, beryl, and micas.

Wolframite is commonly the richest in scandium of the greisen minerals and may contain up to 0.4 percent Sc_2O_3, although the average content is considerably lower. Where wolframite occurs in both greisen and associated high-temperature veins, the scandium content of the wolframite may differ. In the Lake George area, Colorado (Hawley, 1969), wolframite from greisen contained 0.3 percent scandium as compared to 0.07 percent in wolframite from a quartz vein in greisenized wallrock.

Scandium enrichment is uncommon in deposits that would be considered normal hydrothermal veins, and even wolframite and cassiterite from these veins generally do not contain more than 0.005 percent Sc_2O_3 (Vlasov, 1964). Ross and Rosenbaum (1962), however, give an analysis of Colorado ferberite ($FeWO_4$) ore, presumably from the low-temperature hydrothermal veins of Boulder County, that shows a scandium content of 0.01 percent.

VARISCITE DEPOSITS

Sterrettite, one of the few minerals in which scandium is a major component, occurs sparsely in a highly brecciated zone in limestone at Fairfield, Utah. It is associated with a large suite of phosphate minerals of which variscite, $Al(PO_4)_2 \cdot 2H_2O$, and crandallite, $CaAl(PO_4)_2(OH)_5 \cdot H_2O$, are the most common.

In addition to its occurrence in sterrettite, scandium has been found in the associated phosphate minerals, notably crandallite and variscite, which contain from 0.01 to 0.8 weight percent Sc_2O_3. A small amount of scandium oxide was produced from 4,000 pounds of crude ore from the limestone deposit. The ore contained crandallite, variscite, chert, and limonitic clay and averaged 0.10 percent Sc_2O_3 (Frondel and others, 1968).

The deposit at Fairfield is thought to have formed under near-surface conditions by the precipitation of phosphate dissolved by ground water from the overlying Phosphoria Formation (Larsen, 1942). The average scandium content of the Phosphoria is 0.001 percent (Gulbrandsen, 1966), but analyses of phosphatic shale from the Fairfield area were found by Ross and Rosenbaum (1962) to contain as much as 0.05 percent scandium.

Anomalous amounts of scandium have been found in variscite deposits in the Western United States; the origin of the deposits and their relationship to the Phosphoria Formation seems to be quite similar to the origin and relationship of the Fairfield deposit (Frondel and others, 1968), which is the richest deposit found so far.

ENRICHMENTS IN OTHER MATERIALS

Scandium in concentrations greatly above crustal abundance has been found in many geologic materials and mill products, including coals, titaniferous magnetite ores, bauxites, nickeliferous laterites, and some placer deposits (Ross and Rosenbaum, 1962; Vlasov, 1964). None of these sources may be said to constitute a scandium deposit, but some may be considered potential sources of scandium as a by-product of other commodities.

RESOURCES

If an important use developed for scandium that would require tons rather than grams or kilograms of the metal annually, what would be the most logical source? Considering the amount of thortveitite produced from pegmatites in Norway and Madagascar, pegmatite sources would be inadequate. Variscite deposits, such as at Fairfield, Utah, might supply a few pounds, but soon they would be exhausted. It is reasonable, therefore, to consider the lower grade deposits from which scandium might be produced as a byproduct. Tungsten ore concentrates, including concentrates of wolframite, huebnerite, and ferberite, are one important possible source. According to annual reports of the Climax

Molybdenum Co., more than 1,000,000 pounds of tungsten concentrates, containing 0.05–0.08 percent scandium, are produced annually as a byproduct of molybdenum recovery at Climax, Colo. Work by the U.S. Bureau of Mines (Ross and Schack, 1965) has shown that about 85 percent of this scandium is recoverable at a cost relatively modest in relation to the value of scandium. The tungsten ore recovered from this one deposit could thus supply 400–700 pounds of scandium annually.

Uranium deposits, even though they may have a very low scandium content, are potential sources, and indeed some scandium has been recovered from uranium mills in the United States and Australia. Recovery of scandium is made possible by its accumulation in an iron sludge produced in mills which use an organophosphate process for extraction of uranium. This sludge, which may contain 0.1–0.2 percent scandium (Ross and Rosenbaum, 1962), can be treated by methods described by Lash and Ross (1961) and Ross and Schack (1965) to produce scandium oxide. Some scandium was produced commercially from sludge at a uranium mill in Utah, but recovery was discontinued after 1964. Scandium was recovered in Australia from Radium Hill uranium ores. Baroch (1970) stated that uranium ores are the best potential source of scandium, and that as much as 30 pounds a day could be produced from the domestic uranium mills, which were then using the acid leach and clear liquor process.

Phosphorites are another potential source of scandium. Like the rare earths, scandium is released from the phosphate ore during the wet-process production of phosphoric acid. Altschuler, Berman, and Cuttitta (1967) have estimated that 16 short tons of scandium was available for recovery from the phosphoric acid produced from Florida phosphorites in 1964. The phosphorites represent a very large resource of scandium; there are possibly several hundreds of thousands of tons in the world's phosphate deposits (Eilertsen, 1965), but the probability of its recovery from this source seems remote.

The future sources of scandium will undoubtedly be ores of other mineral commodities from which scandium can be recovered as a byproduct. This byproduct status thus ties the resources of scandium directly to those of uranium, tungsten, and phosphate rock, which are discussed in separate chapters of this report.

PROBLEMS FOR RESEARCH

The scandium that is now available as a byproduct but not recovered is irrevocably lost. Under the economic conditions of 1972, it is not likely that any recovery of byproduct scandium will be made unless the demand increases. There is, however, no reason why a few tons of scandium could not be produced annually at less than market value from raw materials now processed in industry. Research into applications for scandium is therefore needed to utilize, rather than lose, the scandium that is currently available. The search for concentrations of the element should continue, not only in natural materials, but also in the waste products of the mineral industry.

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SELENIUM

By H. W. Lakin and D. F. Davidson

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ABSTRACT OF CONCLUSIONS

The present demand for selenium is less than the amount available as a byproduct from the copper industry. Two factors, however, may result in a severe shortage of selenium in the United States in the future. In situ leaching of copper from its ores leaves the associated selenium undissolved in the waste rock resulting from the process. Thus, as the use of the leaching process increases at the expense of smelting, the supply of selenium will decrease. A second and more important factor is the probable increasing use of selenium as a soil additive to provide enough selenium in the diet of domestic animals to insure good health. It is anticipated that this use will require a minimum of 10 times the present annual production of selenium.

Identified resources of copper in the United States are estimated to contain about 52 million pounds of recoverable selenium. About seven times the current annual domestic consumption of 1.1 million pounds of selenium is contained in the coal burned per year in the United States. Thus the most promising source for a greatly increased supply of selenium is as a byproduct for coal-burning powerplants.

INTRODUCTION

Selenium was discovered in 1817 by J. J. Berzelius and J. G. Gahn in a red sediment found in sulfuric acid prepared from the sulfur recovered from pyrite mined at Fahlun, Sweden.

It is a nonmetallic element, of atomic number 34 and atomic weight 78.96, which exists at normal temperatures in two crystalline forms and two amorphous forms. The metastable monoclinic structural form is red, melts at 144°C, has a specific gravity of 4.42, and changes to a hexagonal crystal structure when heated. The stable hexagonal form is black, melts at 220°C, has a specific gravity of 4.82, and conducts electricity—the conductivity increases as much as a thousandfold during exposure to light. A black vitreous amorphous form is obtained by quick chilling of molten selenium. The red amorphous form is obtained by reduction of selenious acid to elemental selenium with sulfur dioxide or other reductant. It turns black on standing.

Of the 1.1 million pounds of selenium used in the United States in 1968, about 40 percent was imported, principally from Canada.

USES

Selenium is commonly marketed as elemental selenium in the form of powder, pellet, and stick in grades varying from 97.00 to 99.99 percent selenium, but it is also available in pellets as very pure selenium—99.999+ percent Se. About 40 percent of the selenium currently consumed in the United States is high-purity grade (99.95–99.9 percent selenium), and it is used in electrostatic printing, rectifiers, exposure meters, photoelectric cells, and optical lenses.

Nearly 30 percent of the annual consumption goes into the manufacture of glass, in which the selenium is used to eliminate the greenish tinge caused by iron impurities. In larger quantities selenium gives a

desirable pink tinge to glass, and in still larger quantities yields a ruby-red glass. Although the principal use of selenium in flat glass is to decolorize, more than 100,000 pounds of selenium per year is used to produce "black" glass that is used as an outer surface in many modern office buildings.

The manufacture of inorganic pigments, principally cadmium sulfoselenide, accounts for about 14 percent of the annual consumption of selenium. These pigments have good light stability and heat resistance and are used in plastics, paints, enamels, inks, and rubber.

The remainder of the selenium is consumed in many diverse applications. For example, selenium added to stainless steels improves their machining characteristics. Selenium compounds are used as vulcanizing agents in rubber products to promote resistance to oxidation and abrasion, and in oils to obtain exceptional antioxidant properties. Selenium and its compounds are used in many catalytic reactions in the preparation of drugs and hydrogenated oils. The element also finds use in fungicides, bactericides, parasiticides, herbicides, and insect repellents and in photographic photosensitizers, phosphorescents, and luminescents. A rather exhaustive listing of uses may be found in the materials survey by Lansche (1967).

An anticipated very large demand for selenium results from the discovery in 1957 that selenium is required in the nutrition of animals, including man. In New Zealand, the addition of selenium to soils to increase the selenium content of forage crops is not only legal but widely done. The use of selenium in fertilizers will probably be legalized in most countries in the near future.

The adverse effects on the economy caused by selenium deficiency are summarized by Oldfield (1971):

> Widespread field occurrence of white muscle disease in lambs and calves, myopathy of the gizzard and heart in turkeys, exudative diathesis in chicks, and liver necrosis in swine, together with depression of growth and decreased efficiency of feed utilization that result from selenium deficiency in commercial feeds, represent heavy economic losses to poultry and livestock producers in many part of the United States. Selenium deficiency diseases with resultant economic losses have also been reported in Canada, New Zealand, Australia, Scotland, Finland, Sweden, Denmark, France, Germany, Greece, Turkey, and Russia. At dietary levels below 0.04 ppm (parts per million) selenium, domestic animals suffer from selenium-deficiency diseases; dietary levels of 1 ppm selenium are completely safe; dietary levels above 4 ppm selenium cause domestic animals to suffer from selenium-toxicity diseases.

Selenium as sodium selenite can be added safely and profitably at the rate of 1–2 pounds per acre once every 5 years in areas where forage crops are deficient in selenium. It is estimated that 12.5 million pounds of selenium per year would be required to treat the most severely selenium deficient areas of the United States; this figure is based on a rate of application of 1.5 pounds of selenium as sodium selenite once every 5 years. To reach an optimum nutritional level of selenium in forage crops in the United States, 25 million pounds of selenium would be needed annually. This consumption would be more than 20 times the amount of selenium used in the United States in 1968.

More selenium would probably be used in industry, especially in steel and glass manufacture, if the supply and price were stable.

GEOCHEMICAL CYCLE

Selenium and its compounds H_2Se and SeO_2 are sufficiently volatile to accompany sulfur in volcanic gases. It has been estimated that approximately 2 pounds of selenium per square yard has been deposited on the earth's surface by volcanic gases. Through this process, selenium tends to become a dispersed element, but other geologic processes tend to concentrate it.

Selenium associated with intrusives accompanies sulfur into sulfide minerals. The ionic radius of Se^{-2} is 1.98 A and that of S^{-2} is 1.84 A; thus Se^{-2} can substitute for S^{-2} in many sulfide minerals. The high-temperature sulfides, pyrrhotite and pentlandite, have a sulfur-selenium ratio of 7,000, a value near that given by Goldschmidt and Strock for the crustal abundance estimate. In sulfide minerals from the mines of the Fahlun area in northern Sweden, the order of decreasing selenium content is galena, chalcopyrite, arsenopyrite, sphalerite, pyrite, and pyrrhotite. The order varies, however, in other areas. In porphyry copper ore containing 0.5 percent copper, the selenium content is 2.5 ppm. In these ores, copper is enriched over its crustal abundance 100 times, but selenium is enriched only 50 times.

In weathering, selenium and sulfur tend to be separated, in large part because selenium becomes fixed in insoluble basic ferric selenites. Only in an alkaline oxidizing environment is selenium oxidized to the soluble selenate form; sulfur, however, is even more readily oxidized to highly soluble sulfate and is carried away in surface and ground waters. As a result, selenium is present neither in sulfate deposits nor in sedimentary sulfur deposits.

In contrast to the separation of selenium and sulfur in weathering processes, the two elements travel

together in biological processes. Selenium replaces sulfur in amino acids; it is taken up by plants and concentrated by some species to a level which can produce toxic effects on animals that eat the plants (Lakin, 1972).

The substitution of selenium for sulfur in biological processes and its reduction to selenides by anaerobic microorganisms often leads to the presence of selenium in pyrite contained in black shales and coal. Selenium is found in pyrite in some unweathered sedimentary rocks and may be found in concentrations many times its crustal abundance in ores rich in organic matter. Highly organic shales may contain as much as 1,500 ppm selenium in selected samples and as much as 20 ppm over expanses of thousands of miles. Phosphorites may contain as much as 300 ppm selenium and are almost without exception enriched above crustal abundance. Brimstones may contain as much as 20 ppm selenium. Coals of the United States average 3.3 ppm (Pillay and others, 1969). The selenium content of soils varies widely, from less than 0.1 ppm to as much as 1,200 ppm.

High concentrations of selenium, to about 1 percent, occur in or with sandstone-type uranium deposits and other similar metal deposits in sedimentary rocks. The selenium is often found in the form of elemental selenium and sometimes as selenide minerals.

Relatively high concentrations (in hundreds of parts per million) occur in tuffs, or tuffaceous rocks, and concentrations of several percent are known in mercury and antimony deposits.

CRUSTAL ABUNDANCE

The abundance of selenium in the earth's crust is still poorly known owing to lack of adequate data. Sindeeva (1964) gave a crustal abundance of 0.14 ppm selenium for rocks of the U.S.S.R. on the basis of the analysis of 18 samples. Brunfelt and Steinnes (1967) found an average of 0.04 ppm selenium in eight standard rock samples provided by the U.S. Geological Survey. Wells (1967) reported an average of 0.6 ppm selenium in 20 volcanic ash samples from New Zealand and 0.4 ppm in lava flows.

Goldschmidt and Strock (1935) estimated that the sulfur-selenium ratio in sulfides is about 6,000 and that the crustal abundance of sulfur is 520 ppm. Dividing 520 by 6,000 gave a figure of 0.09 ppm for the estimated crustal abundance of selenium. This figure was accepted until 1961 when Turekian and Wedepohl (1961) revised the crustal abundance of sulfur downward to 300 ppm and, by using the Goldschmidt and Strock ratio, obtained an estimated crustal abundance for selenium of 0.05 ppm.

RESOURCES

Selenium is obtained primarily as a byproduct of copper refining; 90 percent of the production in the United States is derived from the anode mud deposited during electrolytic refining of copper. Blister copper contains an average of 0.05 percent selenium, or 1 pound of selenium per ton of copper, but actual recovery of selenium ranges from 0.4 to 0.75 pounds per ton of copper. Thus the production of selenium in the United States, and in most of the world, is directly related to the production of copper. In situ leaching processes for the recovery of copper do not result in selenium recovery, and the increasing use of these processes could reduce the supply of selenium materially. Other countries with major potential resources of selenium are those with major potential resources of copper: Chile, U.S.S.R., Zambia, Peru, Zaïre, Canada, and Mexico (Ageton, 1970; see also "Copper" chapter). Minor amounts of selenium are recovered from lead and pyrite ores.

Resources of selenium estimated to be potentially available in the identified resources of copper, lead, pyrite, and coal in the United States and in the rest of the world are shown in table 118.

TABLE 118.—*Selenium resources, in thousands of pounds, potentially available in identified resources[1] of copper ores, lead ores, pyrite, and coal of the United States and the rest of the world*

Source[2]	United States	Other countries
Copper ores[3]	52,000	169,000
Lead ores	880	2,350
Pyrite	560	7,840
Coal	4,740,000	23,760,000

[1] Identified resources: Specific, identified mineral deposits that may or may not be evaluated as to extent and grade, and whose contained minerals may or may not be profitably recoverable with existing technology and economic conditions.
[2] Identified resources from respective chapters of this volume, except for pyrite which is from Lewis (1970).
[3] Assuming 65 percent recovery of selinum.

In electrolytic refining of blister copper, about 65 percent of the contained selenium is recovered from the slime residue. Using the ratio of 0.65 pound of selenium per ton of copper produced, we estimate a total of 52 million pounds of selenium available in identified copper resources of the United States, and 169 million pounds available in identified copper resources of the rest of the world.

Less than 10 percent of the present production of selenium is recovered from lead ores. If it is assumed that galena contains an average of 10 ppm selenium

and the world lead reserves are 140 million tons (see "Lead" chapter), there is a resource of selenium of 3.2 million pounds in lead ores.

Selenium production from the burning of pyrite for sulfur is at present small. The world supply of sulfur in the form of pyrite is estimated to be 375 million long tons (Lewis, 1970). Assuming an average value of 10 ppm selenium in pyrite, there is a reserve of 8.4 million pounds of selenium contained in pyrite.

The average content of selenium in coal is at least 1.5 ppm. Coal resources in the United States are estimated to be 1,580,000 million tons (rounded) and their estimated selenium resource should be 2.37 million tons. Thus, coal contains the major resource for selenium if it can be recovered.

The average selenium content of 86 samples of United States coal from 20 States as given by Pillay, Thomas, and Kaminski (1969) was 3.36 ppm. Eastern coals were higher in selenium content than coals from west of the Mississippi River. Table 119 gives

TABLE 119.—*Selenium content of annual coal consumption at five operating and five proposed powerplants in Western United States*

[Data from Swanson, 1972]

Location	Annual consumption of coal (millions of tons)	Selenium content of coal (parts per million)	Total selenium content of annual coal consumption (pounds)
Operating powerplants:			
Four Corners, N. Mex	7	2.0	28,000
Cholla, Ariz	.4	2.3	1,800
Mohave, Nev	6.7	1.6	21,500
Hayden, Colo	6.25	1.2	15,000
Naughton, Wyo	2.6	.7	3,600
Powerplants planned or under construction:			
San Juan, N. Mex	3.5	2.2	15,400
Navajo, Ariz	8.3	1.6	26,500
Kaiparowits, Utah	15	1.7	51,000
Huntington Canyon, Utah	1	1.7	3,400
Jim Bridger, Wyo	3.8	1.5	11,400
Total	54.5	--	177,600
Average	---	1.65	

the average selenium content of coal used in five existing powerplants and of the coals proposed for use in five powerplants planned or under construction, together with the tonnages used or projected. The average selenium content of these coals is 1.65 ppm. The total selenium in the 54.5 million tons of coal that will be burned in 1 year in these ten powerplants is 177,600 pounds, which amounts to one-sixth of the selenium used in the United States in 1968. The estimated annual release of selenium from the combustion of coal in the United States is about 8 million pounds. The portion of this selenium that escapes into the atmosphere is in, or is rapidly converted to, the form of elemental selenium and is not available to plants or biosystems.

Selenium is enriched in sandstone-type uranium ores and in phosphate rocks mined for their phosphate content. Although some of these ores are relatively high in selenium, they constitute a small source of selenium and have not been exploited for selenium.

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SILICA SAND

By Keith B. Ketner

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ABSTRACT OF CONCLUSIONS

Silica-sand formations and the quartz sandstones from which silica sand and silicon are mainly derived are abundantly distributed throughout the United States and the world. Although the use of silica-sand, principally in the glass and metallurgical industries, is rapidly increasing, shortages that might cause heavy reliance on imports are not likely. Problems are caused if urban development preempts the surface over valuable silica sand deposits and if abandoned sandpits are left in a useless condition. Urban planners can solve the first problem by restricting important sand deposits from other long-term uses, and industry can solve the second by contouring the disturbed surface for productive or recreational use. More detailed geologic investigations in urban areas are needed to precisely delineate silica-sand deposits in advance of urban development.

INTRODUCTION

Natural sands can be composed of siliceous rock fragments and various silica-bearing minerals, but the term "silica sand" is generally understood to mean sand composed almost entirely of SiO_2 in the form of mineral quartz. This type of sand is also called special or industrial sand. Cemented silica sand is called quartz sandstone or quartzite. Some quartz sandstones can be easily broken down to their original state of loose sand either because they were never very firmly cemented or because the cement has been almost entirely dissolved by weathering processes. Sandstones softened by weathering are a principal source of silica sand. Silica sand can be made by crushing and grinding hard quartz sandstones or quartzites, but the result tends to be more expensive than natural sands.

Silica sand of extraordinary purity is required in the manufacture of clear glass and sand of moderately high purity is required in the manufacture of brown or green glass and in certain uses, such as sandblasting, glass grinding, water filtration, railroad traction, and oil-well rejuvenation. Silica sand of moderately high purity with a natural or added bonding material is used in making metallurgical molds and furnace linings. Ground silica sand is a major component of ceramic ware. The use of siliceous raw materials as a source of metallic silicon is not treated here but is discussed by Brantley (1970).

The glass and metallurgical industries consume more than 20 million tons of silica sand per year, and other users consume about 10 million tons. The rate of consumption is increasing rapidly.

Certain relatively expensive natural and artificial aluminous abrasives can be substituted for quartz in blasting sand and glass-grinding sand, but for other uses no satisfactory substitute for high-silica sand has been found.

The quartz content of many impure sands can be raised by beneficiation—the elimination of undesirable impurities such as clay, rock fragments, and iron-bearing minerals. Beneficiation techniques are well known and to some extent are in current use. These include screening, washing with water, leaching with acid, flotation, and various methods that take advantage of differences in specific gravity between quartz and some of the contaminating

grains. The impurities in some sands are themselves valuable when isolated, and their sale can help pay for the cost of beneficiation. Among these are clay and zircon.

Silica sand and sandstone are common rocks of worldwide distribution. Inevitably, any large country that has a varied and representative geologic terrane such as the United States has a large share of these, and the chance that other nations will have deposits distinctly superior to those in the United States is negligibly small. Because of the large resources of silica-rich sand and the opportunities for substitution and for beneficiation of low-grade deposits, the United States should be self-sufficient in silica sand for an indefinite period of time, notwithstanding the fact that a little silica sand is imported occasionally from foreign countries. Importation is the result of very low sea freight rates as compared to the overland freight rates from domestic sources, and it does not reflect adversely on either the quantity or quality of domestic sands.

EXPLOITATION

The annual production of silica sand increased rapidly between the depression year 1932 and 1944, fluctuated around 17 million tons until 1961, and then shot upward. In 1970, the last year for which complete figures are available, production was about 30 million tons, of which one-third was glass sand and one-third was molding sand (fig. 65). The current rate of increase is about 1 million tons per year.

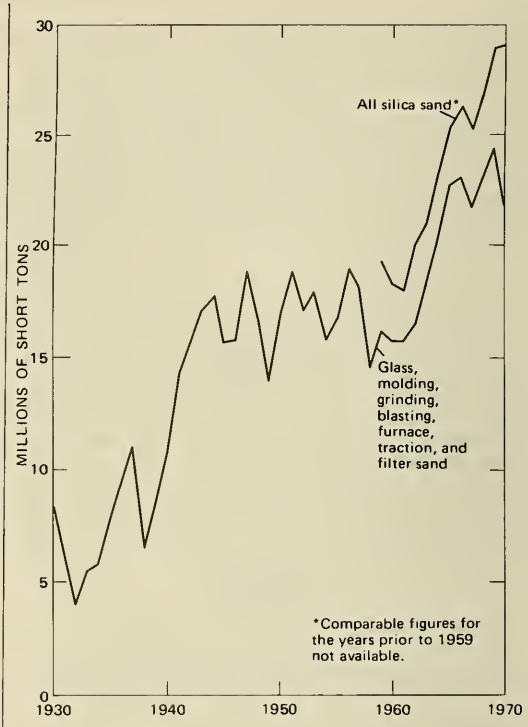

FIGURE 65.—Production of silica sand in the United States, 1930–70. Source of data: U.S. Bureau of Mines.

GEOLOGIC ENVIRONMENT

High-silica sands are the products of especially long continued or often-repeated cycles of weathering, abrasion, and winnowing. The hardness and chemical inertness of quartz work in its favor to form a concentrated quartz sand deposit after almost all other minerals have been reduced to powder and wafted away. The most extensive and purest silica sands were formed in shallow seas. Less extensive and generally less pure deposits were formed as dunes along the shorelines of lakes and the sea, as dunes of desert regions, and as beds and flood plains of streams.

Silica-sand deposits have formed in all geologic periods. Some of the oldest deposits, those of Precambrian age, are very large and very pure but are generally too distant from markets or are too well cemented to compete at present with silica sand from other sources. Many lower Paleozoic deposits are uniquely widespread and pure. For example, the St. Peter Sandstone and related deposits which extend from Wisconsin and Michigan to Oklahoma, an area of more than 300,000 square miles, are composed principally of nearly pure quartz. The Eureka Quartzite and equivalent deposits which extend from Idaho to southern California, an area of more than 100,000 square miles, are likewise composed of nearly pure quartz. Analyses of the Eureka Quartzite indicate that the silica content generally ranges from 95 to 99 percent. The principal commercial deposits of the United States are in locally decemented parts of lower Paleozoic marine sandstones. The process of decementation by which hard sandstone is converted to weakly coherent sand is not well understood, but it is probably the result of local near-surface weathering.

Although many silica sands deposited since early Paleozoic time are widespread and some are very pure, none of them rival those of the early Paleozoic age in extent and purity. Upper Paleozoic sand-

stone in the eastern interior region and upper Mesozoic deposits on the east coast are exploited to some extent, but most outcropping silica sandstones deposited in late Paleozoic and Mesozoic times are located in the western interior States far from industrial users and are therefore not intensively exploited. Marine deposits and dune sands of Cenozoic age are important sources of silica sand along both east and west coasts.

RESOURCES

Silica sand and sandstone are among the more common sedimentary formations cropping out in the United States and, in general, their stratigraphic positions, extent, thicknesses, and the areas of outcrop are among the better known aspects of geology. This is true because silica-rich stratigraphic units generally form conspicuous outcrops, and because some have been investigated as possible oil reservoirs or aquifers. It is unlikely that important silica sand and sandstone units, completely unknown previously, remain to be discovered. Therefore, in a sense, almost all silica sand and sandstone units can be regarded as "identified" rather than as "undiscovered" resources. Parts of these identified resources can be allocated to the category of "reserves." These parts are where certain favorable geologic features fortuitously have combined with favorable geographic circumstances to yield deposits workable under present economic conditions. Favorable geologic features include chemical purity, uniform grain size, friability, amenabiliy to beneficiation, and proximity to the surface. The favorable geographic circumstances are proximity to markets and to transportation facilities.

Identified resources of silica sand are virtually inexhaustible, and reserves are very large in relation to demand. Known deposits can satisfy national demands at reasonable cost for centuries.

PROBLEMS FOR RESEARCH

Although the United States silica-sand resources are so large that they are unlikely to be depleted by normal use, a large proportion of the most favorably located deposits may be precluded from exploitation by shortsighted public policies.

Society's mistakes in this respect can be either unconscious or deliberate—unconscious when residential developments are allowed to spread over valuable sand deposits and deliberate when land-use laws are invoked to prohibit exploitation of known deposits in urban areas. The result of preclusion is not that we will run out of silica sand, but that costs will increase as a result of having to confine mining to areas remote from industrial users and the ultimate consumers.

Sand and sandstone deposits capable of yielding high-quality silica sand should be identified and precisely delineated on geologic maps—especially on large-scale maps of urban regions. Geologic maps exist for many urban areas, but workable silica-sand deposits are specially designated on only a few of these. Precise location of all deposits in urban regions would permit orderly planning for the most beneficial use of land underlain by silica-sand deposits.

If geologic reports are to be of maximum utility for the identification of silica-sand deposits, they must include more quantitative data on the physical attributes of the deposits. Geologic descriptions of sandy stratigraphic units commonly stress only those features that can be seen with a hand lens or microscope. These include grain size, sorting, nature of the cement, proportions of constituent minerals, and the roundness or angularity of the grains. In some reports, care is taken to measure these features quantitatively, but rarely do geologists make enough quantitative observations to permit descriptions of the stratigraphic and regional (three-dimensional) variations in these features. Moreover, general geologic descriptions almost never include important physical features such as coherence and the various factors involved in amenability to beneficiation.

Much of the popular opposition to mining in urban areas lies in the unsightly, dangerous, and useless condition of mined-out areas. Methods for restoring abandoned pits to esthetically acceptable appearance and productive or recreational use should be developed. Most abandoned pits soon fill partially with water. If the banks are sloped and suitably planted and maintained, these ponds can be converted at moderate cost to parks or recreational and wildlife areas.

Although the large resources of silica sand are capable of supporting a rapidly increasing production of disposable glass products (specifically, throwaway bottles), there are valid and pressing reasons for conservational practices. Wasteful consumption will lead inevitably to earlier depletion of nearby high-grade silica-sand deposits and earlier shifts by producers to more distant or lower grade deposits. The direct effect of these shifts will be higher priced glass and more damage to the land surface. The indirect effects will be more pollution in manufacture and, ultimately, more problems in disposing of the product after use.

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SILVER

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ABSTRACT OF CONCLUSIONS

Silver is a major industrial metal in which a major worldwide imbalance of more than 100 million ounces per year exists between production and consumption. The silver used in photography alone in the United States is greater than our annual production, and most of this silver is not recovered for reuse. The deficit between domestic production and consumption formerly was partly filled by withdrawal from the U.S. Treasury silver reserves, but these reserves are now depleted. During the next decade this deficit must be filled by liquidation of private holdings, reclaimed silver, imports, increasing new production, or by use of substitutes for silver.

Identified resources of silver in the United States comprise an estimated 1,440 million troy ounces economically recoverable at present prices (reserves) and an estimated 750 million ounces in material nearly commercial in grade (conditional resources). Other conditional resources that might become recoverable at significantly higher prices are roughly estimated to be of about the same magnitude as the present reserves. Only about 35 percent of the identified resources is in deposits that would yield silver as the main product; the remaining 65 percent would be recovered as a byproduct

of mining copper, lead, zinc, and gold deposits, and its production is thus largely dependent on the production of these metals. For this reason, the imbalance between domestic production and consumption of silver is markedly increased by the permanent closure of one-third of our domestic lead and zinc smelters.

Silver production could be increased by the discovery and development of new silver resources. Among the better possibilities are several kinds of copper-silver deposits such as the northern Idaho-Montana disseminated copper deposits, new porphyry copper deposits, and massive copper-zinc sulfides. Increased prices would encourage development of potential resources in low-grade disseminated silver and copper-silver sandstone deposits and in copper shales, would encourage the reopening of silver-bearing native copper deposits in Michigan, and would encourage the search for manganese-silver and other epithermal silver deposits which could help fill the short-term gap. New environmentally clean smelters and wet recovery methods are needed and must be developed and built as quickly as possible.

INTRODUCTION

Silver is a critical element in our national economy, and one in which our nation and the free world are confronted with a long-range problem of serious imbalance between consumption and new production. Silver is comparatively rare in the earth's crust, being the 67th element in order of natural abundance, but minerals containing it occur in small quantities widely distributed throughout the world in many different types of deposits. The physical properties of silver make it desirable for a wide range of uses for which adequate low-cost substitutes are very difficult to find. It is exceptionally ductile and malleable, it has the highest electrical and thermal conductivity of all metals, its compounds are extremely photosensitive, and it is stable in air and water except for tarnishing readily when exposed to sulfur compounds.

Silver was one of the first metals known to man, and was used for ornaments and utensils made from native silver as early as 3000–2500 B.C. (Ageton, 1970, p. 723). It has been used as a precious metal and as a monetary medium and basis of wealth for more than 2,000 years. It was used extensively for coinage until the late 1960's when such use was discontinued by the United States and most other countries, except for commemorative coins, because of the serious imbalance between consumption and new production. The principal uses of silver are listed in table 120.

Annual mine production of silver in the United States in recent years has been a fairly stable 32–43 million troy ounces of recoverable silver (Hoyt, 1971, p. 1006). In 1969 almost 42 million ounces was produced, which was valued at more than $75 million, an average price of $1.79 per troy ounce (Hoyt, 1971, p. 997). Since then the price had decreased markedly, but by October 1972 had risen to $1.80 per troy ounce. Table 121 gives the mine production of recoverable silver for 1969 in the United States. By far the most important silver-producing State is Idaho—mostly from the Coeur d'Alene district—followed by Arizona, Utah, Montana, Colorado, then by the two midwestern States of Missouri and Michigan which have markedly increased their production. Michigan and Missouri now produce more silver per year than several western "silver" States such as Nevada, New Mexico, South Dakota, and California. Idaho production for 1972 was seriously reduced as a result of the May 1972 fire in the Sunshine mine.

The world production of silver in 1969 is given in table 122. The largest producers of silver were Mexico, mostly from epithermal veins and replacement deposits, and Canada, where the probable largest single source of silver is the Kidd Creek massive sulfide zinc-copper-silver mine at Timmins, Ontario, which has produced between 12 and 14 million troy ounces per year since 1968.

TABLE 120.—*Principal uses of silver*

[Data from U.S. Bur. Mines (1970, p. 1007)]

	Percentage
Photographic materials	29
Electrical and electronic products	22
Sterling ware	20
Electroplated ware	10
Brazing wares	10
Other, including dental and medical products, catalysts, bearings, and jewelry	9

TABLE 121.—*Mine production, in troy ounces, of recoverable silver, 1965 and 1969, in the United States, by States*

[From U.S. Bur. Mines (1970, v, I-II, p. 1006)]

State	1965	1969
Alaska	7,673	2,030
Arizona	6,095,285	6,141,022
California	196,787	491,927
Colorado	2,051,105	2,598,563
Idaho	18,456,809	18,929,697
Kentucky	1,931	----
Maine	----	[1] 319,718
Michigan	457,851	1,009,022
Missouri	299,522	1,442,090
Montana	5,207,031	3,429,314
Nevada	507,113	884,155
New Mexico	287,472	465,591
New York	11,441	31,755
Oklahoma	[2] 358,477	([1])
Oregon	8,801	4,749
Pennsylvania	([2])	([1])
South Dakota	128,971	124,497
Tennessee	94,142	78,614
Utah	5,635,570	5,953,567
Washington	([2])	([1])
Wyoming	52	([1])
Total	39,806,033	41,906,311

[1] Production of Maine, Oklahoma, Pennsylvania, Washington, and Wyoming combined to avoid disclosing individual company-confidential data.

[2] Production of Oklahoma, Pennsylvania, and Washington combined to avoid disclosing individual company-confidential data.

TABLE 122.—*Preliminary report of world mine production of silver, 1969, by countries* [1]

[Data from U.S. Bur. Mines (1970, p. 1010). The letter "e" preceding figures indicates estimated]

Country [2]	Silver (thousand troy ounces)
North and Central America:	
Canada	41,929
Haiti	e 17
Honduras	3,905
Mexico	42,904
Nicaragua	247
United States	41,906
South America:	
Argentina	2,820
Bolivia	6,013
Brazil	357
Chile	3,133
Colombia	77
Ecuador	82
Peru	34,147
Europe:	
Austria	129
Czechoslovakia	e 1,100
Finland	625
France (mine output)	2,000
Germany:	
East	e 4,800
West	e 2,000
Greece	258
Ireland (mine output)	e 1,866
Italy	1,832
Poland	e 165
Portugal (mine output)	339
Rumania	e 800
Spain [3]	e 1,700
Sweden (mine output)	3,683
U.S.S.R.	e 37,000
Yugoslavia	3,456
Africa:	
Algeria	e 100
Congo (Kinshasa)	e 1,896
Ghana	3
Kenya	2
Morocco	861
South Africa, Republic of	3,335
South-West Africa, Territory of [4]	1,273
Tanzania	2
Tunisia	e 47
Zambia [5]	e 768
Asia:	
Burma	e 1,000
China, mainland	e 860
India	127
Indonesia	316
Japan	10,804
Korea:	
North	e 700
South	906
Philippines	1,561
Taiwan	81
Oceania:	
Australia	24,667
Fiji	38
New Guinea and Papua	17
New Zealand	7
Total [6]	288,601

[1] Recoverable content of ores and concentrates produced unless otherwise noted.
[2] Silver is also produced in Bulgaria, Guatemala, Hungary, New Zealand, Thailand, Turkey, and Southern Rhodesia and in several other African countries. Quantities are insignificant or not reported.
[3] Smelter and (or) refinery production.
[4] Recoverable content of Tsumeb Corp. Ltd. concentrates, as reported for year ending June 30.
[5] Includes recovery from copper refinery sludges.
[6] Total is of listed figures only.

Domestic production of silver in 1969 was about 42 million ounces, but industrial use during the same period was about 142 million ounces, leaving a deficit of 100 million ounces; the free world deficit was 124 million ounces (table 123). The marked deficiency of new supplies of silver compared to increased industrial demand, which has nearly doubled for the free world since 1958, has caused major changes in patterns of usage and has forced increases in the price of silver. Until 1971, the deficit in the new supply was balanced by withdrawal of silver stocks from the U.S. Treasury and from sev-

TABLE 123.—*Estimated free-world silver consumption and new mine production, 1949–70* [1]

[Millions of fine troy ounces. From: U.S. Treasury Department staff study of silver and coinage, 1965; 1970 Yearbook of the American Bur. Metal Statistics; and U.S. Bur. Mines (1950–71)]

Period or year	Consumption in arts and industry		Consumption in coinage		Total consumption		New mine production		Free world surplus or deficit excluding coinage
	USA	Total free world	USA	Free world except-ing USA	USA	Total free world	USA	Total free world	
1949–52 (average)	101.1	153.1	36.5	48.2	137.6	237.8	38.8	173.9	+ 20.8
1953–57 (average)	97.8	190.1	37.5	36.0	135.3	263.6	37.7	191.0	+ 0.9
1958	85.5	190.5	38.2	41.3	123.7	270.0	34.1	205.8	+ 15.3
1959	101.0	212.9	41.4	45.0	142.4	299.3	31.2	188.4	— 24.5
1960	102.0	224.6	46.0	57.9	148.0	328.5	30.8	206.9	— 17.7
1961	105.5	239.5	55.9	81.2	161.4	376.6	34.8	203.0	— 36.5
1962	110.4	247.8	77.4	50.2	187.8	375.4	36.8	206.9	— 40.9
1963	110.0	252.2	111.5	55.5	221.5	419.2	35.2	213.8	— 38.4
1964	123.0	285.9	203.0	61.5	326.0	550.4	36.3	215.5	— 70.4
1965	137.0	336.0	320.3	60.8	457.3	717.7	39.0	214.8	—121.8
1966	150.0	355.1	53.8	75.7	203.8	484.6	42.5	222.2	—132.9
1967	145.0	346.8	43.9	61.4	188.9	452.1	31.0	212.8	—134.0
1968	145.0	349.6	37.0	52.3	182.0	438.9	31.7	223.8	—125.8
1969	142.0	364.4	19.4	36.3	161.4	420.1	42.1	240.3	—124.1
1970	135.0	357.6	.7	39.6	135.7	397.9	44.1	254.0	—103.0

eral varieties of hoarded and reclaimed silver. The U.S. Treasury stocks totaled 2.1 billion ounces in 1958, but have since been depleted by transfer to stockpile, redemption of silver certificates, and sales. This depletion of Treasury silver stocks has increased our dependence upon newly mined silver, liquidation of private holdings of silver, and reclaimed silver. Much of the hoarded silver is in coins that have much greater value to coin collectors and speculators than their metal content, unless the price of silver markedly increases. The supply gap of newly mined silver to silver consumption is worldwide, not just domestic, and a large increase in reclaimed silver, release of hoarded silver, and in silver substitutes will be necessary to fill the expected gap within the next decade unless new silver resources are developed. To emphasize current silver needs, the present annual consumption of silver in photography alone is 10 million troy ounces greater than the domestic production prior to the recent decline in mining of western silver-lead ores. Even assuming an increasing replacement of silver by substitutes in the next 30 years, our needs for photography alone will probably increase by 2½ times by the year 2000, to more than 100 million troy ounces per year (Ageton, 1970, p. 734).

EXPLOITATION

Silver has become a major industrial metal and is widely used in the arts. Figure 66 shows the annual U.S. production, consumption, and average price from 1860 to 1972. The more-than 100 million ounces per year gap between U.S. production and consumption is apparent even after the main use of silver for coinage ceased. A smaller but similar gap exists between world production and consumption.

GEOLOGIC ENVIRONMENT

GEOCHEMISTRY

Silver is a chalcophile element; that is, it will combine with sulfur or related anions rather than form silicate minerals. It has a valence of +1 and an ionic radius of Ag^+ 1.13 A. Thus silver is similar in size and valence to copper (Cu^+, 0.96 A) and may substitute for it in various minerals.

The crustal abundance of silver estimated to be 0.07 ppm (parts per million) (Vinogradov, 1962). It is most abundant in basalt (0.1 ppm) and igneous rocks of intermediate composition (andesite and diorite, 0.07 ppm), and slightly less in ultramafic rocks (0.05 ppm) and felsic granites (0.05 ppm). Ore deposits in which silver is mined as a major component are most often associated with igneous rocks of intermediate composition. The silver-lead limestone replacement deposits that occur so extensively in the Western United States are localized near intrusive bodies of quartz monzonite and granodiorite. The rich epithermal silver deposits such as Tonopah and Comstock in Nevada are associated with andesite flows and shallow intrusives or with rhyolite, and the rich silver-cobalt ores at Cobalt, Ontario, and the silver ores at Gowganda, Ontario, and Kongsberg, Norway, are spatially and probably genetically related to diabase intrusives.

Of the world's total production of silver, about 75 percent is a byproduct or coproduct of base-metal ores. In base-metal ores, silver generally has an affinity for galena > chalcopyrite > sphalerite, and the fractionation of silver between coexisting galena and sphalerite ranges from 50:1 to 100:1. Galena is commonly highly argentiferous. Electron microprobe work on Darwin, Calif., galenas by G. K. Czamanske (oral commun., 1972) indicates approximately 0.2 percent (about 60 troy ounces per short ton) can be present in galena with no microinclusions. Experimental studies at elevated temperatures have shown complete solid solutions in the systems $AgSbS_2$–$2PbS$ (miargyrite-galena), $AgBiS_2$–$2PbS$ (matildite-galena), and $AgBiS_2$–$AgMiSe_2$ (matildite-selenium analog) (Wernick, 1960; Van Hook, 1960). Natural galenas from Darwin, Calif., have been analyzed that contained as much as 3.79 percent silver and 7.86 percent bismuth (Hall, 1971, p. 122). Ag^+ and Sb^{3+} or Bi^{3+} thus may form a coupled substitution for $2Pb^{2+}$ in galena at the elevated temperatures of formation of mesothermal ore deposits (about 350°C). Malakhov (1969) tabulated the antimony and bismuth contents of 204 galenas and found that low Sb:Bi ratios are characteristic of high-temperature galena and that high ratios of Sb:Bi are characteristic of low-temperature galena.

In a few lead-zinc deposits, silver is concentrated in sphalerite rather than galena. In the southeast Missouri lead belt, sphalerite contains as much as 45 ounces of silver per ton, probably in solid solution with sphalerite, whereas galena contains about 1 ounce of silver per ton (Hall and Heyl, 1968; Taylor and Radtke, 1969). The geochemical controls for the rare concentration of silver in sphalerite rather than galena are not yet understood.

Silver commonly is greatly enriched in the zone of oxidation, over that in the primary ore, which accounts for many of the shallow bonanza silver deposits that were mined during the latter part of the last century. Only a small part of the primary ore in these deposits was economically minable. Morris and Lovering (1952, p. 698) found at the Tintic Standard mine (Utah) that silver migrates

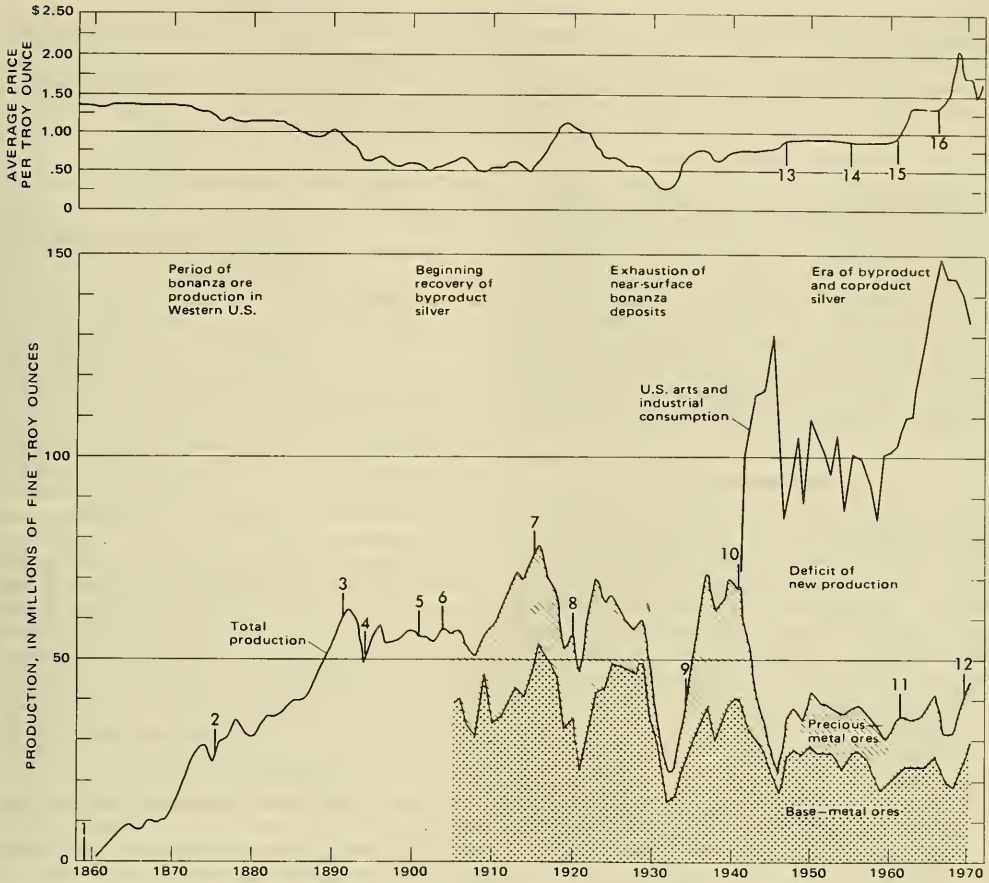

FIGURE 66.—Exploitation of the silver in the United States.

1. Comstock lode, Nevada, discovered;
2. Authorization for coinage of silver dollars;
3. U.S. Treasury act to purchase silver;
4. Purchasing act repealed and sharp price drop;
5. Tonopah, Nevada, discovered;
6. Production began from porphyry copper deposits;
7. Peak from early silver and silver-gold mines and coinage demand of World War I allies;
8. Heavy Chinese buying;
9. Treasury began purchasing silver as monetary backing. Development Silver Belt, Idaho;
10. World War II;
11. Treasury began withdrawal of bullion reserve;
12. Cessation use of silver for coinage;
13. U.S. Treasury directed to purchase domestic silver at 90½c and authorized to sell at 91c;
14. U.S. Treasury sales stabilizes price at 91c;
15. Cessation of U.S. Treasury sales;
16. Exhaustion of U.S. Treasury bullion reserve. Modified from McKnight (unpub. data, 1962).

no more than several feet in limestone and dolomite host rocks but that it is as mobile as zinc in unreactive host rocks such as quartzite and shale. In oxidized lead-silver limestone replacement deposits silver commonly occurs as cerargyrite (AgCl), embolite (AgClBr), native silver, sooty argentite (Ag_2S) or acanthite (βAg_2S), the ruby silvers (proustite, pyrargyrite), silver-bearing lead sulfate, argentian plumbojarosite, argentiferous anglesite, silver-bearing lead carbonate (argentiferous cerussite), various hydrous argentiferous lead-manganese oxides (for example, argentian todorokite), and silver sulfide minerals or sulfosalts precipitated by reaction of silver-bearing solutions with primary sulfide minerals. This supergene enriched ore may carry hundreds or thousands of ounces of silver per ton of ore, but one will be disappointed if one expects such values to continue downward into the primary ore.

MINERALOGY

There are few active mines in the United States whose principal product is silver. Most silver is obtained as a byproduct or coproduct from ores of copper, lead, zinc, gold, manganese, cobalt, nickel, or uranium. There are, however, all gradations from deposits that are mined chiefly for silver to those in which silver is a minor byproduct.

The principal silver minerals are as follows:

- Native elements and alloys:
  - Electrum ——— (Ag, Au)
  - Silver ——— Ag
- Carbonate:
  - Cerussite ——— $PbCo_3$, commonly silver-bearing
- Sulfides, sulfosalts, selenides, and tellurides:
  - Andorite ——— $PbAgSb_3S_6$
  - Acanthite ——— βAg_2S
  - Argentite ——— Ag_2S
  - Diaphorite ——— $Pb_2Ag_3Sb_3S_8$
  - Dyscrasite ——— Ag_3Sb
  - Fizelyite ——— $Pb_5Ag_2Sb_8S_{18}$
  - Galena (argentiferous) ——— $(Pb,Ag)S$
  - Hessite ——— Ag_2Te
  - Matildite ——— $AgBiS_2$
  - Miargyrite ——— $AgSbS_2$
  - Naumannite ——— Ag_2Se
  - Pearceite ——— $Ag_{16}As_2S_{11}$
  - Petzite ——— Ag_3AuTe_2
  - Proustite ——— $(Ag,Cu)_{16}Sb_2S_{11}$
  - Polybasite ——— Ag_3AsS_3
  - Pyrargyrite ——— Ag_3SbS_3
  - Stephanite ——— Ag_5SbS_4
  - Stromeyerite ——— $CuAgS$
  - Sylvanite ——— $Ag_2Au_2Te_8$
  - Tennantite (argentiferous) ——— $(Cu,Fe,Ag)_{12}As_4S_{13}$
  - Tetrahedrite (argentiferous) ——— $(Cu,Fe,Ag)_{12}Sb_4S_{13}$
- Halides:
  - Bromyrite ——— $AgBr$
  - Cerargyrite ——— $AgCl$
  - Embolite ——— $Ag(Cl,Br)$
  - Iodyrite ——— AgI
- Oxides:
  - Aurorite ——— $(Ag_2Ba,Ca,Pb,K_2CuMn^{+2})Mn^{+4}O_7 \cdot 3H_2O$
  - Argentian todorokite ——— $(Ag_2K_2Ca,Ba,Na,Cu,Pb)Mn^{+4}O_9 \cdot 5H_2O$
  - Silver-bearing lead-manganese oxides
- Sulfates:
  - Anglesite ——— $PbSo_4$, commonly silver-bearing
  - Argentian plumbojarosite ——— $(Pb,Ag)Fe_6(SO_4)_4(OH)_{12}$
  - Argentojarosite ——— $Ag_2Fe_6(SO_4)_4(OH)_{12}$

Where silver is a byproduct or coproduct it may occur either as discrete silver minerals or it may substitute for other metals in minerals of base-metal ores. Argentiferous tetrahedrite and tennantite are exceptionally rich in silver in some base-metal deposits, and either one may be the economically important ore mineral. In many lead-silver deposits, silver occurs in tiny inclusions of argentite, tetrahedrite, tennantite, or other silver-antimony or silver-bismuth sulfosalts in argentian galena. Silver may also occur in solid solution in galena. Some galena may be relatively free of silver but accompanied by silver-rich sphalerite, chalcopyrite, and pyrite as in the southeast Missouri lead district (Hall and Heyl, 1968, p. 666). Some sphalerite enriched in silver contains inclusions of argentian tennantite.

Most newly mined gold contains some alloyed silver, the quantity ranging from a trace to as much as 60 percent. Gold from the Mother Lode Belt of California commonly contains 10–20 percent silver; that from the Homestake mine in South Dakota an average of 20 percent. The epithermal precious-metal deposits commonly contain the highest proportion of silver to gold, such as in the Comstock Lode of Nevada.

Placer gold contains less silver than the gold in the lode from which it was derived. Placer gold in California commonly contains 2–7 percent silver, as much as an order of magnitude less than that in the

lodes from which it was derived. The difference has generally been explained as loss of silver during weathering, but Mertie (1940) suggested that in part it may be due to a primary difference between the gold in deep-seated parts of the lode and that in the apical part from which the placer gold was derived.

In addition to silver alloyed with gold, appreciable quantities of silver minerals occur in many gold deposits. Such primary gold deposits grade in many places into predominantly silver deposits, with an increase in silver-bearing minerals such as native silver, tetrahedrite, tennantite, argentite, hessite, pearceite, polybasite, pyrargyrite, proustite, and argentian galena.

Hypogene manganese-silver deposits are widely known. Most commonly they are silver-lead sulfide deposits with associated manganosiderite, such as at Leadville, Colo., or with associated rhodochrosite, such as at Phillipsburg, Mont. D. F. Hewett and his associates recently recognized another type of hypogene manganese-silver deposit, which consists of black silver- and manganese-bearing calcite or of silver-bearing manganese oxides (Hewett, 1964, 1968; Hewett and others, 1963; Hewett and Radtke, 1967; Radtke and others, 1967; and Smith, 1970). In the black calcites, the silver is in intergrowths and inclusions of argentian chalcophanite (aurorite), argentian todorokite, and silver-bearing lead-manganese oxides. The deposits on Treasure Hill, Hamilton, Nev., have this mineralogy.

TYPES OF DEPOSITS

Types of silver deposits are described here under two broad categories: mineral deposits with byproduct and coproduct silver and mineral deposits with silver as a major constituent. Most of the free world's silver comes from deposits of the first category.

BYPRODUCT SILVER

Silver is an important byproduct in (1) porphyry copper deposits, (2) copper-zinc-lead replacement deposits and vein clusters, and (3) massive sulfide deposits; these three types of deposits account for 29 percent of domestic and 20 percent of Canadian silver production. Other types of deposits in which silver is important as a byproduct are (4) lead-zinc replacement deposits, (5) Mississippi Valley- and Alpine-type lead, zinc, and fluorspar deposits and related deposits, (6) copper deposits in sandstones and shales, (7) native copper deposits, (8) gold deposits in veins, conglomerates, and placers, and (9) nickel and magnetite deposits.

These deposits are discussed in this chapter primarily insofar as they relate to production and resources of silver; for more detailed information the reader is referred to the respective chapters on copper, zinc, lead, and gold.

PORPHYRY COPPER DEPOSITS

Porphyry copper deposits are a major source of silver in the United States and supply approximately 20 percent of the domestic production. They are an important source of silver in Chile and to a lesser extent in northern Mexico. Porphyry copper deposits originally were defined as disseminated copper mineralization in felsic porphyritic intrusive bodies, but the term has been broadened generally to include all large, low-grade epigenetic hypogene copper, copper-molybdenum, and molybdenum deposits that can be mass-mined (Titley and Hicks, 1966; see also chapter on "Copper"). Although the percentage of silver in the ore is very low—about 0.01–0.1 ounce of silver per ton of ore—the total amount of silver that is recovered is very significant because of the vast tonnages mined. The porphyry molybdenum deposits, on the other hand, are virtually free of silver except for trace amounts. During 1970, the Bingham open-pit mine in Utah, a copper-molybdenum deposit, was the fifth largest silver producer in the United States, with an output of 2.6 million ounces of silver from 40 million tons of ore, or 0.065 of an ounce of silver recovered per ton of ore (Lindstrom, 1971). Arizona contains the largest known concentration of porphyry copper deposits. Fourteen such deposits average 0.06 of an ounce of silver recovered per ton of ore (8 ounces of silver per ton of copper). Known "predicted" resources of porphyry copper deposits in Arizona are estimated to be 80 million tons of copper (A. F. Shride, oral commun., 1972) from which an estimated 640 million ounces of silver can be recovered.

In recent years, porphyry copper deposits that contain silver have been found in Puerto Rico; in Maine near Jackman, along the Quebec border; in British Columbia; and in Panama. The deposits in Puerto Rico are relatively lean in silver and contain only a few parts per million of silver per ton of ore (D. P. Cox, oral commun., 1972). Most are not yet being mined. Porphyry copper deposits and copper-molybdenum deposits are now in production in British Columbia. Porphyry copper deposits in Chile annually yield about 3½ million troy ounces of silver. Similar deposits in Peru also produce silver. The newly discovered porphyry copper deposits in Irian, Bougainville, New Guinea, and Iran will probably

constitute important new silver sources in the future.

Few porphyry copper deposits are known in Asia and Africa, and none are known or developed in Europe. Extensive low-grade porphyry copper deposits in the Balkhash-Kourmadskiy area of the eastern part of the U.S.S.R. contain silver, but only the shallow enriched zones are productive at present. A small but rich porphyry-type copper deposit is being mined in syenitic rocks and carbonatite at Palabora, northeast Transvaal, Republic of South Africa.

COPPER-ZINC-LEAD REPLACEMENT DEPOSITS AND VEIN CLUSTERS

Silver is an important byproduct or coproduct of some copper-zinc-lead replacement deposits such as at Butte, Mont., and in the Johnson Camp, Turquoise, Banner, and Superior districts, Arizona. In these, the copper generally is in a central zone which is surrounded by low-temperature zones of galena and sphalerite. At Butte, a peripheral zone contains manganese. Silver is enriched in the peripheral zones compared with the central copper zone. The ore bodies may be veins; irregular, pipe-shaped, or bedded replacements; or stockworks. The predominant primary copper mineral is chalcopyrite, although bornite, chalcocite, covellite, djurleite, and enargite are important minerals at Butte.

Butte yielded more than 644 million ounces of silver between 1880 and 1964—the second largest producer of silver, after Coeur d'Alene, in the United States. The ore occurs in veins within the Boulder batholith, with a central zone of copper deposits, an intermediate zone of copper-zinc deposits, and a peripheral zone with zinc, lead, silver, and manganese deposits (Meyer and others, 1968). Total production of silver at Butte has averaged about 2 ounces per ton of ore mined, about half of which is from the central Berkeley Copper Pit, the remainder from the outer part of the intermediate zone or from the silver-rich copper-zinc-lead peripheral zone. Total production at Butte has averaged about 1 ounce of silver for each percent copper, and current production is about 0.3 of an ounce of silver for each percent copper (Meyer and others, 1968, p. 1376).

The copper and copper-zinc replacement deposits in Arizona are mainly in limestone or altered limestone host rock near granitic intrusive bodies. The Magma mine has consistently produced 300,000 to 1 million ounces of silver annually from ore that has averaged 1.93 ounces per ton (Hammer and Peterson, 1968, p. 1286), largely from the steep, east-striking Magma vein. This vein has been developed over a strike length of 10,000 feet and to a depth of 4,900 feet.

The Kennecott copper mine in the Copper River region, Alaska, produced about 12 million ounces of silver during almost continuous operation from 1911 to 1938. The copper ores, which contained 14 to 16 ounces of silver per ton, occurred in replacement veins, in irregular massive replacements, and in stockworks in partly dolomitic beds in the Chitistone Limestone of Triassic age, which overlies thick copper-bearing basalts. The copper and silver was mainly in chalcocite and covellite (Bateman and McLaughlin, 1932).

At Gilman, Colo., copper-silver-gold ores fill fractures, coat vugs, and replace early massive pyrite bodies in chimneys at the lower end of mantos. The ores average 3.5 percent copper, 18.7 ounces of silver, 0.08 of an ounce of gold per ton.

In the southern part of the Tintic district in Utah, copper-silver-zinc-lead deposits include fissure veins and wallrock replacements of enargite, sphalerite, and silver minerals near Silver City, and the great replacement pipes and mantos of copper-arsenic-silver ores in the southern parts of the Mammoth mine.

In the Eastern United States, ores of this type are uncommon, and but few are known. The Barrett prospect, East Pembroke, Maine, is a stockwork of copper-zinc-silver ore in metavolcanic rocks. In the Linganore district of the Maryland Piedmont, chalcopyrite and bornite containing some silver, and locally argentian galena and sphalerite, are in veins and replace marble along contacts with metavolcanics.

MASSIVE SUFIDE DEPOSITS

The term "massive sulfide" as used here follows the definition of Anderson and Creasey (1958, p. 96): " * * * deposits consisting of a granular aggregate of sulfide minerals such as pyrite, chalcopyrite, sphalerite, and galena, with little or no visible gangue minerals." Many contain pyrrhotite, magnetite, arsenopyrite, tetrahedrite, and barite, and many contain silver and gold as important byproducts. The geology and genesis of massive sulfides related to volcanic belts has been discussed by Anderson (1969), and is summarized in the "Copper" chapter of this volume.

Massive sulfide deposits are of tremendous worldwide commercial importance as sources of silver and base metals in Canada, Japan, Ireland, Cyprus, Australia, U.S.S.R., Spain, Sweden, Philippines, Turkey, West Germany, and Norway. Some of the largest

productive mines in North America that supply silver as a byproduct are massive sulfide deposits. They are abundant in the following regions: (1) The Appalachian region of the United States and Canada (Bathurst, New Brunswick; Buchans and Tilt Cove, Newfoundland; Maine and Vermont; Ducktown, Tenn.) (Kinkel, 1967; Heyl and Bozion, 1971); (2) the Precambrian Shield of eastern and central Canada (Kidd Creek, Timmins, Ont.; Noranda, Quebec), including the Adirondack uplift in New York and the Wisconsin dome in Wisconsin and Michigan; (3) the Pacific coast region of California (Kinkel and Hall, 1952), British Columbia, and Alaska; and (4) the Basin and Range province and Rocky Mountains (Iron King, Bagdad, and Jerome, Ariz. (Anderson, 1969), Pecos, N. Mex., and the Sedalia mine, Colorado).

At the United Verde mine, Jerome, Ariz., 57 million ounces of silver was recovered between 1883 and 1952 (Anderson and Creasey, 1958, p. 101). This represents 2½ ounces of silver per ton of ore, or 31 ounces of silver per ton of copper. The Iron Mountain mine, in the West Shasta district, California, was first mined for silver in the gossan, which locally averaged about 8 ounces of silver per ton of ore; the primary ore contained less than 1 ounce of silver per ton (Kinkel and Albers, 1951, p. 8). The massive sulfide deposits with substantial amounts of sphalerite and galena carry more silver than the pyrite-chalcopyrite ore. At the Iron King mine, Arizona, the ore averaged 4 ounces of silver, 2.2 percent lead, and 6.4 percent zinc (Anderson and Creasey, 1958, p. 155). At the Mammoth mine, California, the massive sulfide ore that was mined for copper contained 2.2 ounces of silver whereas the ore mined for zinc averaged 5.8 ounces of silver per ton (Kinkel and Hall, 1952, p. 6).

LEAD-ZINC REPLACEMENT DEPOSITS

Lead-zinc replacement ore deposits are one of the principal sources of silver. Most argentiferous lead-zinc replacement deposits formed from hydrothermal solutions of deep-seated origin at the margin of or within intrusive bodies of granitic to dioritic composition. In the margins of the intrusive bodies, limestone is a particularly favorable host rock, but quartzite, argillite, and schist also host major deposits. Many deposits are localized near or within the intrusive by structural features such as a favorable bed near a feeder fissure, a fracture or fissure, a brecciated zone near the intrusive, or a favorable bed in a roll in the structure. Especially favorable geologic settings are found near Mesozoic and Tertiary instrusives in the circum-Pacific belt and near Tertiary intrusives in the Great Basin and Rocky Mountains, eastern Canada, and central Europe.

Much of the rich silver ore is produced from lead-silver-zinc replacement deposits in limestone. These include such famous camps as Park City and Tintic, Utah; Leadville and Red Cliff, Colo.; Silver City and Magdalena, N. Mex.; Eureka, Nev.; and Cerro de Pasco and Casapulca, Peru. The bedded replacement deposits at Park City are in many places contiguous with vein deposits that occupy feeder fissures in which the ore solutions moved. Silver-rich lode deposits were exploited in the early years of the district. The Ontario lode provided high-grade silver ore over a strike length of approximately 5,000 feet and to a depth of 1,300 feet (Barnes and Simos, 1968, p. 1116). Where the vein is in the Weber Quartzite, it contains high-grade ore, but in the underlying limestone the ore is discontinuous and lower grade. Extensive bedded limestone replacement ore bodies are found in the overlying Park City Formation; these deposits have been the major source of production since the early exploitation of the high-grade lodes. The Jenney limestone bed of economic usage, which is 100 feet above the Weber Quartzite-Park City Formation contact, is the host rock for most of the large bedded deposits (Garmoe and Erickson, 1968, p. 34). It was mineralized over a strike length of more than 6,000 feet, with a maximum width of 150 feet, and ranged in thickness from 25 to at least 100 feet. The ore averaged 25.3 ounces per ton of silver, 14 percent lead, and 12 percent zinc.

At Tintic, Utah, much of the ore mined during the early history of the district averaged 30–40 ounces of silver per ton (Lindgren and Loughlin, 1919, p. 105–112) and some of it assayed more than 100 ounces per ton. At Darwin, Calif., much of the near-surface primary ore averaged 50 ounces of silver per ton whereas the deeper replacement ore averaged about 6 ounces per ton (Hall and MacKevett, 1962). Oxidation and supergene enrichment of these argentiferous galena ores produced the shallow-depth bonanza ore bodies that were mined during the latter part of the 19th century.

Lead-zinc deposits with appreciable silver occur in quartzite, argillaceous rocks, and schist, as veins or veinlike replacements along steep fissures or in fractures along bedding. Veins of this type constitute much of the formerly productive mineral belt of Colorado, particularly in the Montezuma, Idaho Springs, and Silver Plume districts, where they occur in fault zones in Precambrian gneisses (Lovering and Goddard, 1950, p. 138–178).

MISSISSIPPI VALLEY- AND ALPINE-TYPE LEAD, ZINC, AND FLUORSPAR DEPOSITS AND RELATED DEPOSITS

The Mississippi Valley-type districts contain epigenetic, low-temperature, hydrothermal deposits of galena, sphalerite, and pyrite, and locally fluorite, barite, chalcopyrite, calcite, and cobalt minerals. These deposits have been productive in lead, zinc, fluorite, and barite, and some have produced copper, silver, cobalt, and nickel as byproducts. The lead in the galena is of the radiogenic Joplin type (J-type). Brown (1970) has prepared an excellent summary of the geology and characteristics of the Mississippi Valley-type and related deposits. At present, about 2 million ounces of silver per year is produced from the southeast Missouri district, which makes it one of the major silver-producing districts in the United States. Most of the silver is recovered from sphalerite, from some of the chalcopyrite, and from a silver-lean galena. Silver is not recovered from other sulfides, such as pyrite, although locally they contain some silver.

Silver is present in small amounts in both sphalerite and galena in the Upper Mississippi Valley district. Analyses of 29 sphalerite samples range from 0.03 to 10 oz of silver per ton and average 0.7 oz per ton (Bradbury, 1961; Hall and Heyl, 1968). Analyses of 33 samples of galena range from 0.05 to 3 oz of silver per ton and average 0.58 of an ounce per ton.

Silver is recovered from some of the galena concentrates in the Illinois-Kentucky district, where silver in galena ranges from 15 ounces per ton of concentrates in Illinois to about 5 ounces per ton in western Kentucky (Hall and Heyl, 1968). In many veins, fluorite ores were mined, and galena and sphalerite-rich ores remain. Only traces of silver are known in the rest of the Mississippi Valley-type districts, but in many of them almost nothing is known of the silver content of minerals.

The Appalachian Valley zinc deposits contain little lead. Where galena is present, it contains some silver in the range of 1–2 ounces per ton; the lead in it is not notably radiogenic. Silver has been recovered from the deposits in the Embreeville, Tenn., and Austinville, Va., districts.

In many respects the lead-zinc deposits of the Alps in eastern France, Austria, northern Italy, and Yugoslavia resemble the Appalachian Valley zinc deposits except that in the Alps the galena is much more abundant than sphalerite. In all of these countries some silver in the galena is recovered as a byproduct, but the deposits are not notably rich in silver. The lead isotopes in the galena are notably radiogenic in thorium lead (B-type).

Ore deposits in the Metaline district of northeastern Washington occur as large, irregular replacement bodies in the Middle Cambrian Metaline Limestone. Sphalerite and galena are the ore minerals; chief gangue minerals are jasperoid, dolomite, coarse calcite, and pyrite. Practically all the zinc and lead has been mined from an irregular zone near the top of the Metaline Limestone known as the "Josephine horizon" that is characterized by widespread brecciation. Other zinciferous zones are known in the Metaline Limestone but have not been exploited. Production from the district for the last few years has been at the rate of about 200,000 tons annually with a grade of 2.31 percent zinc, 0.85 percent lead, and 0.036 of an ounce of silver per ton. Total production of silver through 1969 amounts to 657,109 ounces. The potential resources of the "Josephine horizon" may be as much as 1.2 million tons of lead, 3.4 million tons of zinc, and 5.3 million ounces of silver (Weissenborn, 1966).

Somewhat similar deposits are found immediately to the west in Stevens County, Wash. As at Metaline, the deposits form replacement bodies in the Middle Cambrian Metaline Limestone; zinc predominates over lead; and the silver content of the replacement deposits is low but the total silver production is substantial—incomplete data suggest that it amounts to about 600,000 ounces.

COPPER DEPOSITS IN SANDSTONES AND SHALES

Blankets or lenses of disseminated copper ores, in places with associated silver, and less commonly with lead, zinc, cobalt, vanadium, and uranium, are found throughout the world in marine and continental shallow-water sandstones and shales. Most of these deposits have no apparent association with igneous rocks. The silver is mostly in chalcocite, djurleite, argentite, bornite, and chalcopyrite, and their oxidation products, but some is native silver. Some of the deposits are very large, such as the upper Precambrian stratiform blanket deposits in shale near White Pine, Mich., and the Permian carbonaceous copper shales of Mansfeld (Germany), Poland, and the U.S.S.R. Copper shales in Poland contain 80–750 ppm silver. Copper shales near Kornberg, West Germany, contain about 1.5 percent copper and 10 ppm silver. Copper shales at White Pine contain more silver than those at Kornberg. The resources of White Pine are very large; more than a million ounces of silver per year is currently produced as a byproduct of the White Pine deposits, in addition to the silver needed to produce the White Pine silver-bearing Lake-brand copper, which contains 12 ounces or more of silver per ton. A much

smaller quantity of silver comes from southwestern Oklahoma deposits.

Lenticular, bedded, and roll deposits of disseminated chalcocite and pyrite, that locally contain uranium and vanadium minerals, occur in sandstones, mostly of Mesozoic age, in eastern New Mexico, southeastern Colorado, and in the Colorado Plateau province of Colorado, New Mexico, Utah, and Arizona (Fischer, 1937). Similar deposits are known in northeastern Utah, southern Idaho, and northeastern Pennsylvania. Most of these deposits are lean in silver, but contain small quantities in ores that have been mined for their copper content. Silver might be recovered from such ores in the future.

Disseminated chalcocite, bornite, covellite, and chalcopyrite, locally with a little native copper and silver, occur in beds, veins, breccia zones, and along dikes in sandstones of Triassic age in Connecticut, New Jersey, Pennsylvania, Maryland, and Virginia, and in the Cashin mine in southwestern Colorado (Emmons, 1906), and in nearby deposits in Utah.

The existence of possible economic concentrations of copper in beds of the Precambrian Belt Supergroup has been generally recognized only recently. (See chapter on "Copper.") One deposit has been developed to the point where it could be mined when desired, and other prospects are in various stages of exploration. These deposits are said to average about 1 percent copper and to contain about 2 ounces of silver per ton for each percent of copper. Much work remains to be done before any realistic forecast can be made of the silver resources of the Belt Basin. They obviously could constitute an important resource of both silver and copper. Company exploration geologists stated (A. E. Weissenborn, oral commun., 1971) that the expected size of individual deposits may be as much as 60–100 million tons.

NATIVE COPPER DEPOSITS

Very large deposits of native copper and associated native silver occur in amygdaloidal basalt flows and conglomerates on the Keweenaw Peninsula, northern Michigan; probably they were deposited by heated chloride-rich brines that rose updip from beneath the present location of Lake Superior (White, 1968). The deposits have been productive from prehistoric times until 1970, when the last mines were closed after having yielded nearly 5.4 million tons of copper and a very substantial quantity of silver. Most of the silver production was not recorded, however, because it was retained in the "Lake copper" produced, which contains as much as 8 ounces of silver per ton. The remaining resources in this district are very large, but mostly low grade, and are awaiting better metal prices and improved mining and recovery methods.

GOLD DEPOSITS IN VEINS, CONGLOMERATES, AND PLACERS

Silver is alloyed with gold in all precious-metal deposits. The amount of silver is indicated by the fineness of the gold, which is the proportion of gold to silver expressed in parts per thousand (thus, for example, "900 fine" means a gold to silver ratio of 9:1, or 10 percent silver). Mesothermal and hypothermal gold-quartz veins generally have more gold than silver, whereas the epithermal precious-metal and the shale and sandstone deposits have more silver than gold.

Gold-quartz veins are found extensively in metamorphic terranes around the world: in Western United States and Alaska; in the Precambrian shield of Canada and the United States; at Victoria, Australia; and in the Precambrian areas of South Africa, the Ural Mountains, the Austrian Alps, Brazil, India, and Siberia.

The most extensive gold-quartz veins in the United States are in California along the belt of Mesozoic granitic rocks. The most productive was the Mother Lode Belt, which extends for a distance of 130 miles on the west side of the Sierra Nevada batholith in a folded belt of metamorphosed Paleozoic and Mesozoic volcanic and sedimentary rocks. The Mother Lode is a vein system with individual veins as much as 1 to 2 miles long; some veins have been mined 5,000 to 10,000 feet down the dip.

The gold-quartz veins in the Kirkland Lake and Porcupine districts in the Canadian Shield have many similarities to the Mother Lode veins. They occur in tightly folded Keewatin andesite and basalt flows, and the mineralogy of the veins is simple. The silver to gold ratios range from 0.11 to 0.25.

The Homestake mine, South Dakota, produced approximately 28 million ounces of gold and 6½ million ounces of silver between 1878 and 1965, a gross of nearly $1 billion at today's prices (A. L. Slaughter, in Ridge, 1968, p. 1437). The ore occurs as a replacement of isoclinally folded Precambrian Homestake Formation (Hosted and Wright, 1923), and consists of several percent of pyrrhotite, arsenopyrite, and pyrite in a calcite-quartz-chlorite-ankerite gangue.

Other important deposits of gold-quartz veins in the United States that have yielded byproduct silver include those in the Colorado mineral belt, the Appalachian Piedmont gold belts in the southeastern United States, the Neihart district, Montana, Mogollon district, New Mexico, Wallapai district, Arizona, the London vein system, Alma district, Colorado, and

the Gold Mountain quartz veins in Tertiary tuffaceous sediments, pyroclastics, flows, and associated intrusives in the Republic district of Washington have yielded about 7½ million ounces of silver as a byproduct of gold mining. Epithermal gold-quartz veins in silicified zones in the Paleocene Swauk Formation at Wenatchee, Wash., have also yielded considerable byproduct silver.

Gold-bearing conglomerate deposits in the Witwatersrand district, Transvaal, South Africa, have yielded more gold than the total gold produced in Alaska, California, and Colorado. Similar conglomerates have been mined in West Africa at Tarkwa and Abosso. The fineness of the gold in two Witwatersrand mines ranges predominantly from 750 to 925 (Von Rahden, 1965, p. 983).

All placer gold contains byproduct silver, although the amounts in the gold are much smaller than in the nearby lodes, and the total quantity per placer is small. The placers on the west side of the Sierra Nevada, and near Fairbanks, Alaska, and the Yukon, Canada, however, have yielded appreciable quantities of silver. Future production of large amounts of silver from gold placers is unlikely because of the low grade of the remaining gravels and because of environmental considerations.

NICKEL AND MAGNETITE DEPOSITS

About a million ounces of silver is produced annually from the nickel ore bodies at Sudbury, Ontario. (See chapter on "Nickel.") The silver occurs in small amounts in chalcopyrite, and in galena of the mineralogically more complex "offset deposits," which are probably hydrothermal. Production is expected to continue for many years.

At Cornwall and Morgantown, Pa., silver is recovered as a byproduct, along with gold, copper, and cobalt, from high-temperature hydrothermal magnetite deposits. (See chapter on "Iron.") The silver occurs in small quantities in chalcopyrite that is common in the ores. A small but steady output has come from these deposits for many years. Although Cornwall is approaching exhaustion, Morgantown is a major new mine and is expected to continue production.

SILVER AS A MAJOR CONSTITUENT

Mineral deposits in which silver is the main constituent include a wide variety of types, and they constituted some of the most productive deposits in the notable districts that were mined in the 19th century. They are no longer very productive except in a few major districts. These silver-rich deposits are (1) epithermal veins, lodes, and pipes, (2) epithermal disseminated and breccia deposits, (3) epithermal silver-manganese deposits, (4) epithermal silver-lead-zinc replacement deposits, (5) epithermal silver-copper-barite deposits, (6) mesothermal silver-lead-zinc-copper deposits, (7) mesothermal cobalt-silver, cobalt-uraninite-silver, and cobalt-silver-zeolite deposits, (8) sandstone silver deposits, and (9) sea-floor muds and hot-spring deposits.

EPITHERMAL VEINS, LODES, AND PIPES

Epithermal veins, lodes, and pipes form within a few thousand feet of the surface, under slight load, and generally in brittle rocks where open fractures and cavities are abundant. They are formed by deposition of silver-bearing minerals from hot ascending solutions in areas of volcanic activity. The presence of anomalous amounts of arsenic, antimony, mercury, bismuth, tellurium, and selenium are good geochemical indicators of favorable areas for prospecting and exploration. They are distinguished from mesothermal and hypothermal deposits by small grain size, open cavities, crustification, banding, and comb structures. They most commonly occur in Tertiary volcanic flows or tuffs, generally andesitic to rhyolitic in composition, or in fault fissures between these and other rocks. Only rarely do they occur in basalt, or in the underlying or adjacent rocks of plutonic or sedimentary origin. The common ore minerals are argentite, pyrargyrite, polybasite, and other complex silver sulfosalts, argentiferous tetrahedrite, argentiferous galena, and sphalerite. Most of the deposits contain gold, either free or alloyed with silver as electrum, and base-metal sulfides that are seldom of economic importance. Many of the deposits contain cerargyrite and native silver as secondary minerals in the zone of oxidation. The gangue minerals include quartz, and typically less abundant adularia, calcite, dolomite, barite, and fluorite, and rarely, rhodochrosite and rhodonite. Wallrock alteration is generally well developed and marked by abundant kaolin, chlorite, carbonate minerals, and pyrite, and locally by sericite or zeolites. The ore bodies commonly occur as shoots or chimneys of richly mineralized vein material surrounded by lower grade ore or barren gangue minerals. They are generally confined to fault fissures and other fractures but may locally extend into the wallrocks. The ore bodies range widely in size and grade; some have been mined continuously for strike lengths of several thousands of feet, and have yielded ore that contained from a few ounces to many thousands of ounces of silver per ton. Few deposits are known to extend to depths of more than

2,000 feet below the surface, and most are confined to less than 1,000 feet below the outcrop.

The most famous epithermal silver deposit in the United States, and perhaps the world, is the Comstock Lode in western Nevada (Becker, 1882; Bastin, 1922; Gianella, 1936; Thompson, 1956). This great deposit yielded nearly a half billion dollars in gold and silver from ore bodies along a strike length of about 3 miles and to a depth of more than 2,000 feet. Another notable epithermal vein deposit is the Hornsilver, in the San Francisco district of Utah (Butler, 1913). This giant vein of silver-bearing galena, sphalerite, argentite, pyrargyrite, and chalcopyrite lies in a large fault between Tertiary quartz-latite flows on the east and lower Paleozoic limestone on the west. The vein was rich in silver, lead, and gold where partly oxidized near the surface; as in many epithermal veins, the productive part extended to only about 1,000 feet. Other notable epithermal vein deposits in the United States are those at Tonopah (Nolan, 1935) and Austin (Ross, 1953), Nev.; Mojave (Tucker, 1935) and Randsburg (Hulin, 1925), Calif.; and the Mogollon district, New Mexico (Anderson, 1957). Many of the rich silver deposits of Mexico and the Andes belong to this type. The eastern part of the Harz vein district in West Germany contains epithermal silver-lead veins with a wide variety of silver minerals.

Epithermal precious- and base-metal veins and lodes in Tertiary andesitic breccia of the San Juan Mountains of Colorado contain both silver and gold. Major silver-producing mines are still active in the Telluride-Sneffels district, near Silverton, and at Creede, where the host rocks are mostly felsic volcanic rocks. Most of the deposits in the San Juan Mountains are within or near the margins of giant calderas (Steven, 1968). At Creede, a new vein system recently opened up by the Homestake Mining Co. contains an unusual native silver and copper sulfide ore. Farther north this vein probably grades into very coarse grained, vuggy, argentiferous galena, sphalerite, and copper minerals similar to the Holy Moses, OK, and Amethyst veins to the east (Steven and Ratté, 1965).

In the Silver Cliff and Querida districts of south-central Colorado, breccia pipes in rhyolite are cemented by rich crusts of galena, sphalerite, various silver minerals, free gold, and gold tellurides. The best known deposits are those of the Bassick and Geyser mines. Nearby is the Bull Domingo pipe with mineralogically similar ore that cements a Tertiary breccia formed in Precambrian rocks. The deposits are small, but locally rich. Near Silver Cliff, a volcanic basin is covered by a blanket of altered rhyolite with many small intersecting silver veins. Beneath part of the district is a large, low-grade, epithermal porphyry-type silver-lead-zinc-copper deposit which is a resource for the future.

EPITHERMAL DISSEMINATED AND BRECCIA DEPOSITS

The large deposit at Calico, in southeastern California (Wright and others, 1953), has yielded about $20 million in silver from barite veins along faults and from rich pockets of cerargyrite, embolite, and native silver in shattered volcanic rocks and lake beds of Miocene age. Few of the deposits extend to depths greater than 200 feet. Exploration in 1966 indicated a disseminated silver deposit containing many millions of tons of low-grade silver-bearing material in faulted and brecciated sedimentary rocks of late Miocene age along the Calico fault zone.

The Monitor district, California, also has low-grade disseminated silver in braided fissure zones in altered andesite of Miocene-Pliocene age. The silver occurs as argentite, polybasite, and pyrargyrite. Similar deposits are reported in Nevada and Arizona.

Silver-antimony-lead-bearing epithermal jasperoid reefs that replace limestone were mined in the Taylor and Success districts east of Ely, Nev. (Drewes, 1967). Similar ores, of silver, occur in jasperoid mantos in the Vipont district in the northwest corner of Utah. Many other small deposits of this type are known in Colorado, Utah, and Nevada.

EPITHERMAL SILVER-MANGANESE DEPOSITS

Silver-rich manganese carbonate, manganiferous black calcite, and manganese oxide deposits, occurring as veins in layered volcanic rocks and as replacement deposits in limestone, were briefly productive in the United States. The best known districts are Lake Valley, N. Mex.; Pioche, Tybo, and White Pine, Nev.; Escalante, southwestern Utah; Tombstone and Aquila, Ariz.; Silver Cliff, Colo.; and Modoc, Calif. In these and numerous other similar districts in the west, the silver mineral mined was cerargyrite that occurred in small near-surface deposits; the hypogene silver minerals were not determined in most deposits (Hewett and others, 1965; Hewett and Radtke, 1967). The most recently developed deposit of this type is in the Escalante district near Modena, Utah. Here a large tonnage of 10- to 15-ounce silver-manganese ore has been developed in a large vein of manganese oxides, fluorite, black calcite, vanadinite, pyromorphite, descloizite, and wulfenite; the vein, in rhyolite, extends below the shallow water table without sulfides. In the White Pine district, Nevada, the cerargyite ores are worked out, but aurorite, argentian todorokite, and hydrous

silver-bearing lead-manganese oxides have been identified from black silver-bearing manganiferous calcite samples (Radtke and others, 1967).

One of the richest of the oxidized silver-manganese deposits was mined in the Lake Valley district, New Mexico, from 1878 to 1893, during which time it yielded 5 million ounces of silver (Jicha, 1954, p. 71). Half of the silver came from one stope where the silver occurred in cerargyrite and one 4-foot face averaged 15,000 ounces of silver per ton. Lower grade silver ore consisted of silver-bearing manganese and iron oxides in cherty limestone. The nature of the primary ore is not known inasmuch as all the mined ore was manganese oxides and silver chlorite in limestone; only a small amount of galena, almost completely oxidized, was found. Sulfide cavities are uncommon.

EPITHERMAL SILVER-LEAD-ZINC REPLACEMENT DEPOSITS

Epithermal silver-lead-zinc replacement deposits are not common, but a few have been very productive. One of the largest and most productive districts with such deposits is Aspen, Colo., where large veins and replacements along bedding-plane faults and cross faults in Mississippian carbonate rocks contain large, rich, pocketlike hypogene ore bodies of barite, pearceite, and native silver near the surface. In places these bodies grade into fine-grained colloform silver-rich galena and sphalerite. Other silver replacement deposits occur at Eureka and Cortez, Nev.; Tombstone, Ariz.; Hermosa and Kingston, N. Mex.; and Shafter, Tex.

Variants of this type are the Tertiary volcanic breccia pipes or chimneys of silver, gold, lead, zinc, copper, and tungsten ores that formerly were productive in the Red Mountain district in the core of the Silverton caldera of the San Juan Mountains, Colo. (Burbank and Luedke, 1968). The ore was deposited at shallow depth and replaces the breccia, or it forms cylindrical replacement envelopes around the pipes along the contact with wallrocks and fills the interstices. These epithermal ores are rich in silver and copper, and in places include pipes of shallow-depth high-temperature deposits containing heubnerite. The best silver ore consists mostly of stromeyerite and bornite.

At Mercur, Utah, the Carlin-type very fine grained limestone-shale gold-arsenic replacement ores grade into silver ores geologically similar to the Carlin, Nev., gold ores. The first mining was for silver, and the gold ore was found after the highest grade silver ore had been mined out and the camp abandoned for a decade (Gilluly, 1932).

EPITHERMAL SILVER-COPPER-BARITE DEPOSITS

Rich silver-copper-barite deposits of Triassic age were found in the 1960's at Walton, Nova Scotia (Boyle, 1963; 1972). At the surface, pipe deposits were mined for barite and manganese. Subsequent deep drilling for barite revealed deposits, beneath the barite in the same pipe, that consist of chalcocite and at least 10 other copper and silver sulfide minerals. Similar barite deposits with silver-bearing chalcocite are known in the Triassic shales of the Connecticut Valley. Hewett (1968) suggested that the Walton deposit is a type of silver occurrence that might be expected beneath the manganese-silver ores previously mined.

MESOTHERMAL SILVER-BASE METAL VEINS

The Coeur d'Alene district of Idaho is the country's leading silver producer, one of the few active mining districts in the world in which a significant part of the ores are mined chiefly for their silver content. Through 1968 its mines have yielded approximately 754,300,000 ounces of silver, 7,010,000 short tons of lead, 2,555,000 short tons of zinc, and 125,000 short tons of copper, in addition to substantial amounts of cadmium and antimony. The total value of the metals produced exceeds $2.3 billion.

The ore is in replacement veins in weakly metamorphosed argillites, siltites, and quartzites of the Precambrian Belt Supergroup. Coeur d'Alene ore shoots are characteristically longer in vertical dimension than in horizontal dimension. Ore has been mined over a vertical range of 8,000 feet. Many ore shoots have been bottomed, but others continue below the lowest mine levels, with no evidence to suggest their bottom limit. The principal producing mines are found in two groups, one north of the Osborn fault, the other south of the fault. The eastern part of the southern group is known as the "Silver Belt" because of the higher silver content of the ore.

In most mines in the Silver Belt, the ore averages about 25 ounces of silver per ton and 0.75 percent copper. In the other mines the combined lead-zinc content averages 10–12 percent, and the silver content is variable.

The Chewelah district, which has been the leading producer of silver in Stevens County, Wash., is in an entirely different geologic setting from the Coeur d'Alene district. The silver is in braided quartz-carbonate veins in shear zones in argillite of the Belt Supergroup. Chalcopyrite is the principal ore mineral. All the mines are within 2 miles of outcrops of the Flowery Trail Granodiorite (Clark and Miller,

1968). The district has yielded 1,747,000 ounces of silver and 5,350 tons of copper, mostly from the United Copper mine. The mines have been idle for many years, and it is unlikely that mining will be resumed under present or foreseeable conditions.

MESOTHERMAL COBALT-SILVER, COBALT-URANINITE SILVER, AND COBALT-SILVER-ZEOLITE DEPOSITS

The cobalt-silver veins of Cobalt, Ontario, have yielded about 500 million ounces of silver to date, and several mines have been revived in recent years. The deposits occur in thin, short, vertical veins in diabase sills about 1,000 feet thick. The main minerals are native silver, cobalt, nickel and iron arsenides, arsenic sulfides, dolomite, and calcite. Some galena, chalcopyrite, pyrite, sphalerite, pyrrhotite, and tetrahedrite are present. Typical high-grade ore averages 10 percent silver, 9 percent cobalt, 6 percent nickel, and 39 percent arsenic (Jones, 1953, p. 18). The origin of the silver veins is controversial. Many believe the silver source was in the magma that gave rise to the diabase. Others suggest the ore minerals or metals were derived from sedimentary rocks interbedded in the greenstones.

Similar deposits on the east shore of Great Bear Lake, northwestern Canada, contain native silver, cobalt and nickel arsenides, chalcopyrite, some uraninite, and bismuth, in thin quartz veins. The principal economic mineral in some veins is uraninite, and in others, native silver. Gangue is altered host rock, quartz, carbonates, and hematite. Five stages of mineralization have been recognized; pitchblende is part of an early stage and native silver is part of the latest stage.

The Echo Bay mine, opened in 1964, has produced nearly 16 million ounces of silver. In 1971, this mine produced about 2.5 million ounces of silver and 650,000 pounds of copper. Mill heads average 70 ounces of silver per ton and 0.95 percent copper (Northern Miner, Jan. 6, 1972). Four large masses, largely of silver, that weighed 1,620, 800, 412, and 344 pounds were mined in August 1971; the largest mass contained about 70 percent silver.

Deposits somewhat similar to those at Great Bear Lake were formerly quite productive at Kongsberg, Norway; and at Andreasberg, Annaberg, and Schneeberg in Saxony, Germany. These deposits contain native silver, silver sulfides, cobalt, bismuth, and nickel arsenide associated with lead and zinc sulfides. Uraninite is much less abundant in these deposits than at Great Bear Lake although locally the veins are enriched in uraninite. Zeolites, barite, fluorite, calcite, and ankerite are the main gangue minerals. The veins at Schneeberg are ore bearing in metamorphic clay-slates but are impoverished in the underlying granite. The veins are multistage: the nickel-cobalt-bismuth ores are associated with an early stage; uraninite with an intermediate stage; and silver with a late stage.

SANDSTONE SILVER DEPOSITS

Silver chloride deposits disseminated in sandstone occur in southern Utah at Silver Reef (Proctor, 1953). Small ones are also found to the southwest near St. George. The mines, which were productive for about 20 years in the late 19th century, yielded nearly 8 million ounces of silver.

The deposits are a silver-rich variant of the Colorado Plateau sandstone uranium deposits and the sandstone copper-silver deposits previously described (Fischer, 1937). Most of the Silver Reef deposits contain some copper and, locally, some uranium and vanadium. The ore bodies are restricted to the Silver Reef Sandstone Member (of Proctor, 1953) of the Upper Triassic Chinle Formation and occur in blankets and lenses on the limbs and nose of a major anticline. The ore bodies were emplaced prior to anticlinal folding. They tend to be richest in carbonaceous trash pockets and in cross-bedded sandstone beds and lenticular channels. The silver is mostly in cerargyrite, but it occurs locally as native silver. Associated minerals are malachite, azurite, and locally carnotite. Trace-element studies indicate that silver bromides are probably also present. The ore minerals are essentially invisible and occur as micrograins cementing the sandstone grains, and as thin gray crusts on lignite. Pyritic concretions, now altered to limonite, locally are especially rich in silver. The ores were worked to the water level and the mines closed. Little exploration was done below the water table, although the geology suggests that unoxidized ore, similar in grade to the oxidized ore, should be present. Little search has been made for similar ores elsewhere in the Colorado Plateau.

SEA-FLOOR MUDS AND HOT-SPRING DEPOSITS

Mineralized sea-floor muds of the Red Sea contain lead, zinc, and iron sulfides, and some silver in lenticular blankets in local basins (Degens and Ross, 1969). They are being deposited by heated brines rising through the sea floor in the central part of the Red Sea. The blankets, which are very large, are examples of mineral deposits being deposited at present by hydrothermal solutions. Such deposits may ultimately form massive sulfide blankets such as those at Meggen, West Germany.

Near Niland, Calif., close to the Salton Sea, a very

concentrated brine with an unusually high content of potassium, lithium, and heavy-metals was tapped by a deep well that was drilled for geothermal power (White and others, 1963, p. 919–922). Evaporated residue of a deep water stream sample indicates the original water contains 1,000 ppm manganese, 2 ppm silver, 100 ppm lead, 500 ppm zinc, and 20 ppm copper. Dark material deposited in the discharge pipe from the well contained a high concentration of copper and silver. Such silver-bearing fluids might deposit their metal content to form syngenetic silver deposits in such closed saline basins as the Salton Sea.

RESOURCES

IDENTIFIED RESOURCES

Listed in table 124 are our estimates of silver reserves and identified resources of material nearly commercial in grade and of hypothetical silver resources (undiscovered but geologically probable resources in known districts) in the United States. They are subdivided by geologic type of deposit as previously described.

The total of identified resources is about 2.2 billion troy ounces, half again as large as the reserve of 1.4 billion ounces estimated in 1968 (table 125). The difference between these two estimates is attributed partly to the discovery of the large disseminated silver-copper deposits in the Precambrian Belt Supergroup in northern Idaho and western Montana, which at present constitute a conditional resource, and partly to the increased potential resources in porphyry copper deposits. We have not attempted to estimate conditional resources in detail, but such resources that might become recoverable with a threefold to fourfold increase in the price of silver are roughly estimated to be of about the same magnitude as the present reserves.

Hypothetical resources are based on geologic evidence for assumed continuations or repetitions of deposits in similar geologic settings.

The identified resources of byproduct silver are nearly twice those of silver as the main product, and the hypothetical resources of byproduct silver are more than 15 times those of silver as the main product. By far the greatest silver resources are in porphyry copper deposits, massive sulfides, and copper-zinc-lead veins and replacement deposits, but very large identified resources are contained in the silver-rich lead veins and replacements such as those in the Coeur d'Alene district, Idaho; in the lead-zinc-silver replacement ores such as those at Leadville, Colo.; and in silver-bearing epithermal veins, lodes, and pipes similar to those in the San Juan Mountains of Colorado. Resources in the southeast Missouri district are surprisingly large, because although the percentage of silver in the ores is small, the tonnages of ore are immense. The small hypothetical resources of silver in ores in which it is a main

TABLE 124.—*Silver resources (in troy ounces in ores) in the United States*

Type of deposit	Identified resources[1]	Hypothetical resources[2]
Deposits in which silver is a byproduct		
Porphyry copper deposits	741,000,000	725,000,000
Copper-zinc-lead replacements and veins and copper-bearing sandstones and shales	398,000,000	1,585,000,000
Massive sulfide deposits	8,000,000	81,000,000
Lead-zinc replacement deposits	170,000,000	235,000,000
Mississippi Valley-type deposits	54,000,000	50,000,000
Alpine-type zinc deposits in Valley and Ridge province	200,000	200,000
Native copper deposits	50,000,000	500,000,000
Gold veins and placers	5,000,000	35,000,000
Other types	2,000,000	2,000,000
Total	1,428,200,000	3,213,200,000
Deposits in which silver is the main product		
Epithermal veins, lodes, and pipes	128,000,000	93,000,000
Epithermal disseminated and breccia deposits	12,000,000	11,000,000
Epithermal manganese and barite deposits	18,000,000	18,000,000
Epithermal replacement deposits and mesothermal veins with lead and zinc	605,000,000	69,000,000
Mesothermal cobalt-uraninite-silver deposits	0	1,000,000
Sandstone silver deposits	2,000,000	10,000,000
Total	765,000,000	202,000,000
Total byproduct plus main product silver resources	2,193,000,000	3,415,000,000

[1] Identified resources: Specific, identified mineral deposits that may or may not be evaluated as to extent and grade, and whose contained minerals may or may not be profitably recoverable with existing technology and economic conditions.

[2] Hypothetical resources: Undiscovered mineral deposits, whether of recoverable or subeconomic grade, that are geologically predictable as existing in known districts.

TABLE 125.—*Silver reserves,[1] in millions of troy ounces, of United States and free world[2]*

	Silver reserves		
	Measured and indicated ore	Inferred ore	Total
United States	590	850	1,440
Free world (including U.S.)	3,200	2,200	5,400

[1] Reserves: Identified deposits from which minerals can be extracted profitably with existing technology and under present economic conditions.

[2] Compiled in 1968 by E. T. McKnight and T. H. Kiilsgaard, U.S. Geological Survey, from all available published data, records of government agencies, data provided by mining company personnel and by minerals attachés, and annual reports of mining companies, based on materials considered economically exploitable at or near 1965–68 metal prices.

product reflect the fact that most such deposits are restricted to shallow depth, and thus have small vertical extents.

Silver consumption in the United States and in the world will probably continue to greatly exceed the newly mined supply, because silver is, and will continue to be, a byproduct or coproduct of copper, lead, zinc, and gold ores, and therefore its supply depends largely upon the production of these metals. In the future, silver will probably be produced more from the many types of copper deposits and from zinc-rich, lead-lean massive sulfides than from the silver-lead-zinc replacement and gold deposits that supplied most of the silver in the 20th century. The marked decline in western silver-lead and zinc production will continue because the high-cost western mines and smelters cannot compete with eastern ore until new, more efficient mining and recovery methods are commercially developed (which will take at least 5–10 years), and until the price of silver is high enough to assure that the western silver industry will once more be competitive. A rise in the silver price would aid the opening of low-grade disseminated silver deposits such as those at Calico, Calif. Opening of more porphyry copper deposits and of large, recently developed silver-bearing copper deposits in sandstone and shale, such as the disseminated copper-silver deposits of Idaho, Montana, Michigan, Oklahoma, and New Mexico, will partly fill the gap.

Imported silver comes largely from Canada, Mexico, Peru, Ireland, and Australia. Most of the Canadian deposits are copper- or zinc-rich massive sulfides, silver deposits, gold deposits, or porphyries. The Mexican deposits are largely silver-rich epithermal and replacement deposits and copper porphyries. Those in Peru are copper porphyries and silver-lead deposits. The deposits in Australia and Ireland are largely massive sulfides. Increased production from these foreign deposits to obtain more silver in the immediate future will seriously affect our balance of payments and the present balance between supply and demand of base metals.

HYPOTHETICAL RESOURCES

The potential resources of silver will be increased substantially when economic conditions will justify exploration for large, low-grade deposits.

Stratabound copper deposits may be a very large worldwide potential resource of silver that is not yet widely exploited except in Poland, East Germany, and Michigan. The existence of possible economic concentrations of copper and silver in the sandstones and shales of the Precambrian Belt Supergroup in Montana and Idaho, for example, has been recognized only recently. An enormous potential resource with more than 0.2 percent copper and 0.4 of an ounce of silver per ton is suggested by current investigations of the Belt Supergroup, and a hypothetical resource of 1 billion ounces of silver is possible. In addition, anomalous amounts of copper are known in sedimentary or low-grade metasedimentary rocks of Belt age in Africa, Australia, Russia, and Canada (Harrison, 1972, p. 1232). The southwest Oklahoma copper shales are known to extend at depth throughout most of the Anadarko Basin, eastward across much of Oklahoma, and northward into Kansas, and to grade into silver-rich deposits in southeastern Oklahoma. The sandstone silver deposits of Silver Reef, Utah, are probably a variant of the Colorado Plateau uranium and copper-uranium deposits, many of which contain some silver. New sources are probable among the hundreds of uranium prospects not rich enough to be mined, where silver is a trace element and copper is common. The Silver Reef ore minerals are so nearly invisible that new deposits will not be found without careful sampling and analysis. Small sandstone silver deposits are known elsewhere in southwest Utah, indicating that Silver Reef is not unique.

Massive sulfides, which are the source of so much of the world's base- and precious-metal ores, are abundant in the Appalachian Mountains. Under favorable economic conditions, many new commercial ore bodies can probably be found by prospecting and following prospects along known belts of metavolcanic rocks. A similar possibility for new deposits exists in the Precambrian of the Basin and Range province, outward from the well-known deposits in Arizona into central New Mexico, and northward into Colorado and southern Wyoming. These three States have large areas of exposed Precambrian rocks that contain many small massive sulfide deposits which have been largely overlooked because of the nearby Laramide and Tertiary deposits. The Sierra Nevada foothills in California and the northern California Shasta deposits are similar promising areas to search. A point worth remembering is that in 1950 the great massive sulfide deposits of Bathurst (New Brunswick), Gaspé (Quebec), Timmins (Ontario), and Newfoundland were unknown, but their presence was marked by small, nearly forgotten prospects of sulfide, which had been discounted and ignored by exploration geologists for many years.

SPECULATIVE RESOURCES

The United States, including Alaska and Puerto

Rico, probably contains more silver-bearing deposits than almost any other nation in the world, and is one of the most favorable of nations for potential discovery of new deposits. The search for new deposits should be nationwide and not just restricted to the West. Perhaps one of the greatest silver anomalies in the United States is in southeast Missouri, and the Appalachian Mountain belt contains many silver occurrences of many geologic varieties. Large parts of Alaska are favorable for silver deposits, but the limited accessibility has discouraged intensive exploration. The Western United States has so many districts that it is still considered prime "prospecting ground."

Perhaps one of the most promising of the speculative resources which includes silver is the possibility that massive sulfides of the Japanese Kuroko type may occur in the young volcanic belt of the Aleutian Island chain of western Alaska, and along the adjacent mainland. Geologically, this volcanic region is almost ideal for Kuroko-type volcanogenic massive sulfide deposits, and such deposits should be present somewhere in this long chain of islands.

The geology of the German and Polish copper shales should be studied as examples in the search for similar shales in the United States. The European shales lie in a Permian saline basin with permeable sandstones above and below. Beneath them in the basins are thick salt, potash, and gypsum-anhydrite beds. During deposition the basins were shallow and were surrounded by subdued metamorphic uplands that contained many mineral deposits. The copper shales are in thin beds (6–8 in. thick) of black carbonaceous shale that are mineralogically zoned and that grade laterally into lead-, zinc-, and silver-rich strata. Copper shales containing silver are now mined in southwest Oklahoma. Similar copper shales may occur unrecognized in many other places in the United States where shallow, nearly closed basins previously existed.

More than half the Basin and Range province is covered by alluvial deposits; many of the basins are largely pediment surfaces with thin gravel covers, beneath which much of the geology is similar to that of the adjacent mountain ranges. Many different kinds of silver-bearing deposits could exist in these basins at shallow depths. Exploration problems to be solved are much like those of glacial drift-covered shield areas. At present, geochemical prospecting is one of the best tools for finding them.

Large Precambrian shield regions are covered by thin glacial deposits and thin Paleozoic sedimentary covers in northern New York, central and northern Wisconsin, upper Michigan, northern Minnesota, and eastern South Dakota. For years the geology of central and northern Wisconsin was shown as a great green undifferentiated area on the State geologic map because of the thick glacial cover and the sparseness of outcrops. This map (now being replaced) did not show the detailed and meticulous unpublished surveys of the geology completed prior to 1920. Dutton and Bradley (1970), in cooperation with the Wisconsin Geological and Natural History Survey, compiled maps and field-checked the outcrops indicated by the old unpublished notes. Several metavolcanic belts were delineated, and in them, large massive sulfide copper deposits have been found. Similarly, detailed mapping by Brown (1970) located a small deposit of sphalerite in a marble belt west of Balmat, N.Y., in the same rock as the major Balmat-Edwards zinc-lead deposits. Outcrops of the Balmat and Edwards ore bodies were quite small and not very promising (J. S. Brown, oral commun. to Heyl, 1967). Discoveries of similar small outcrops of mineral deposits in the region could lead to the discovery of major new ore bodies. Similar studies are warranted in the other Precambrian shield areas of the United States.

The Carlin-type epithermal gold deposits are nearly unrecognizable in the outcrop, as no gossans exist in the slightly altered limestones. At Mercur, Utah, a similar deposit produced much gold ore, but also some silver ore. Carlin-type epithermal silver ores may occur elsewhere in Utah, Nevada, Arizona, and New Mexico. They can be found only by careful geochemical analysis of slightly altered limestones and shales.

Because of the major importance of porphyry copper deposits as a source of silver, the reader is referred to the excellent discussion of speculative resources of porphyry copper in the "Copper" chapter of this volume. Almost all outcropping deposits in the Western United States have probably been tested, but the recent discovery at Catheart Mountain, Maine, suggests that a whole new eastern belt of porphyry copper deposits is possible in the Appalachian Mountain belt from Newfoundland to Alabama; and recent discoveries in Puerto Rico and Panama point to new regions of possible discoveries in the Caribbean.

The andesitic belts of the United States should be geologically mapped and reexamined for silver-bearing deposits. Ancient Precambrian belts of the West and Midwest should be located beneath glacial drift and the thin capping of Paleozoic sedimentary rocks. The use of statistical geochemical prospecting, geologic drilling, and the tracing of glacial boulder trains are also suggested. Where this has recently

been done, as in north-central Wisconsin, some important discoveries have been made.

During the 1960's, a large, low-grade disseminated silver deposit was explored by drilling and trenching in faulted areas in the Miocene Barstow Formation and in the formation at Burcham in southern California. The exploration work indicates the potential for large, low-grade silver deposits that could be mined at low cost in the vicinity of the former bonanza epithermal deposits. Such deposits may occur in other places in the West and they constitute a potential for large-scale mining during periods of good silver prices.

The sandstone silver deposits at Silver Reef, Utah, were worked only to the ground-water table. If they are variants of the Colorado Plateau uranium deposits, as the geology indicates, the deposits could change into primary silver sulfide ore below the water table. The mineralogy and form of this hypothetical primary ore is unknown, but if it is similar to Plateau uranium ores, it should be in blankets and rolls, should be similar in grade to the ore above the water table, and should be concentrated in fluvial channels near pyrite concretions and carbonaceous trash pockets.

The discovery of many mixed base- and precious-metal massive sulfide deposits in Ireland in the 1960's indicates a strong possibility that similar ores occur in the almost identical geologic setting along trend in Scotland and northern England. Similarly, if continental drift and ocean-floor spreading is a valid concept, Newfoundland should have many more lead-zinc-silver massive sulfides than have already been found. Boulders of massive sulfide ore are common in the glacial drift derived from the interior of the island.

The work of Hewett and his associates (Hewett, 1968; Hewett and others, 1965; Hewett and Radtke, 1967) on primary epithermal manganese-calcite and manganese-silver deposits has indicated the likelihood of finding silver ores under many of the western (and some Appalachian) epithermal manganese oxide deposits. Similarly the Walton, Nova Scotia, barite deposits change to silver-copper-barite ores at depth. This change indicates that all eastern Triassic barite, as well as all copper and manganese deposits in the United States, should be reexamined with a similar possibility in mind.

Another potential source of silver and base metals is the mineralized sediments that occur in thermal deeps, such as the Red Sea basin (Degens and Ross, 1969). According to Bischoff and Manheim (1969, p. 535), the uppermost 10 meters of the Atlantic Deep in the Red Sea contains 50 million tons of mineral-bearing sediment averaging 1.6 ounces of silver, 3.4 percent lead, 1.3 percent copper, and 0.10 percent zinc. Old basins that had similar hot-spring activity, such as the Mississippi River embayment of the Coastal Plain and the Salton Sea region in the Gulf of California, should be reexamined for possibilities of similar deposits.

PROBLEMS FOR RESEARCH

Without question, major new resources of silver can be located and developed in the United States if the need increases, if prices for silver and other metals improve, and if the general industrial climate is favorable for the production of silver. The present decline in silver production will probably continue for years, however, until new, more efficient mining methods and cleaner recovery methods are developed. The smelters that have closed, or are about to close, are old and obsolete, and are almost impossible to bring up to present environmental-control standards. New wet methods and bacterial recovery methods may be part of the answer to cleaner recovery methods, if the silver is recovered along with base metals, but some of the answer must be in new smelters in which controls for fumes and ash are built in when the plant is constructed. A tall stack to catch the dust and disperse the fumes is no longer a sufficient control.

The recent emphasis in mining methods has been on mass production from huge open pits that are largely permanently destructive to large acreages of land in the West, even if partly reclaimed. Yet some of the largest, most efficient, lowest cost mines in the country are underground operations, which if properly planned have much fewer permanent environmental problems. Further improvements and breakthroughs are needed in techniques of underground mining, and the surface plants should be made attractive and relatively permanent, as they are in most European countries and in Japan.

The mineralogy and accepted natural occurrences of silver should be reevaluated. Silver minerals are notably difficult to identify in the field and by the older mineralogic methods. In part, this is because they commonly occur in microscopic-size crusts, grains, and inclusions. Silver-free and silver-rich types of sphalerite, galena, tetrahedrite, and copper sulfides look alike. Analysis is commonly the only way to determine the presence of silver, and sensitive methods like atomic absorption or the electron microprobe must be used to detect trace amounts.

Traditionally, ores rich in galena, chalcopyrite, tetrahedrite, and mixed complex sulfide and sulfosalt ores are analyzed for silver, whereas sphalerite,

pyrite, smithsonite, and chalcocite ores are not generally so analyzed. Silver-rich sphalerite is mined in southeast Missouri and in the Nigadoo mine in the Bathurst district of New Brunswick; silver-rich chalcocite is mined at White Pine, Mich., and is common in the sandstone chalcocite ores of Connecticut and near Walton, Nova Scotia. Silver-rich pyrite was thrown on the dumps of the Milan massive sulfide mine in New Hampshire; silver-rich smithsonite ores were found in several districts in Colorado, Utah, Nevada, and California, but the silver was seldom recovered because the silver content was not recognized. Analyses for silver should be made in these and in many other common minerals from the waste material in old mining districts as well as in all new discoveries.

Minerals bearing silver, such as the manganese oxides, or chlorides, iodides, and bromides, have been automatically classed as supergene minerals wherever found. Hewett (1968) has shown that hypogene silver-manganese oxide minerals are common at one locality, and they have been identified elsewhere in the West (Hildebrand, 1967). Cerargyrite, embolite, and other silver halides theoretically could be deposited as hypogene minerals as well as supergene; these minerals are notably difficult to identify. They might occur in closed lake basins where chloride brines are present to precipitate silver from silver-bearing hot-spring solutions, such as those found at the edge of the Salton Sea in southern California.

As the lead-zinc industry becomes increasingly dependent on eastern low-cost silver-lean lead and zinc, silver production will probably depend increasingly on copper-silver deposits of the several types and upon silver-rich ores in which silver is the main product. With the gap increasing between silver production and consumption, another search for epithermal silver deposits is probably warranted, using the newly developed geochemical and geophysical prospecting techniques.

The recovery of more byproducts will help support production of marginal ores. Valuable elements now wasted, such as manganese, bismuth, germanium, tellurium, and tin, as well as silver might be recovered by new and better metallurgical techniques.

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SULFUR

By Alfred J. Bodenlos

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ABSTRACT OF CONCLUSIONS

Sulfur, an element in wide industrial use, currently is mined or recovered in the United States from elemental sulfur deposits associated with evaporites, from sulfur-bearing petroleum and natural gas, and from sulfide ores. The element also occurs as a constituent in bedded gypsum and anhydrite, coal, tar sands, and oil shale, as well as in volcanic deposists, none of which is being used at present as a domestic source of sulfur. Reserves are appreciable and resources are vast, not only in the United States but in many other parts of the world.

Elemental sulfur is formed as a product of anaerobic bacterial activity wherever both sulfate ions and organic material are abundant; therefore, areas of potential sulfur discovery include anhydrite units in any petroliferous evaporite basins. Most accumulations of petroleum and natural gas high in sulfur content also are found in evaporite basins. Sulfide ores, in contrast, occur in a wide variety of rocks in all parts of the world. Volcanic sulfur occurs mostly in the circum-Pacific belt, but it also has been found in volcanoes extending from the Mediterranean to the Himalaya Mountains.

Most countries contain sulfur-bearing accumulations in one form or another, but few contain large deposits of elemental sulfur. The extraction of sulfur from such accumulations in any given country depends largely upon recovery costs, which must be competitive with the prevailing world price of elemental sulfur.

INTRODUCTION

Sulfur, a soft yellow mineral that melts at 113°C, has broad industrial use. Most sulfur is used in the manufacture of sulphuric acid, and only a relatively small amount is used in elemental form, as sulfur dioxide, or as carbon disulfide. The world's sulfur

reserves and resources are irregularly distributed; the commodity, therefore, moves in large tonnages in international trade (Ambrose, 1965; Lewis, 1970; Lundy, 1949; and Fogarty and Mollison, 1960).

In approximate order of increasing cost of mining or recovery, the following raw materials provide most of the world's sulfur and sulfuric acid supply:

1. Elemental sulfur deposits in evaporite rocks.
2. Hydrogen sulfide contained in sour natural gas.
3. Organic sulfur compounds contained in petroleum.
4. Massive deposits of pyrite.
5. Elemental sulfur deposits in volcanic rocks.
6. Ores of metallic sulfide minerals (Cu, Zn, Pb, Ni, Mo).

Additional large resources of sulfur occur in the following minerals or compounds:

7. Beds of the calcium sulfate minerals, anhydrite and gypsum.
8. Organic sulfur compounds in tar sands.
9. Organic sulfur compounds and pyrite in coal beds.
10. Organic sulfur compounds and pyrite in oil shale and shale-rich organic matter.

Approximately one-quarter each comes from elemental sulfur, massive pyrite, and sulfur in oil and gas. Only the elemental deposits in evaporites or in volcanic rocks are mined solely for their contained sulfur. Pyrite deposits can be mined for their sulfur, as the chief product or as coproducts or byproducts from the production of iron and other metals. Sulfur is recoverable from all the other types of deposits only as a byproduct or coproduct that can be used directly in acid manufacture or converted to elemental sulfur for shipment elsewhere. Sulfur contained in the last seven types of raw materials, however, commonly is lost to the atmosphere either during processing or through use of the primary product.

Sulfur and its chemical compounds are used in virtually every segment of the world's industrial and agricultural complexes, as shown by the almost perfect parallelism between the Federal Reserve Board index of U.S. industrial production and the sulfur demand index (Landsberg and others, 1963). Principal uses in the United States are in the manufacture of soluble fertilizers, synthetic fibers, plastics, papers, pigments, explosives, petroleum products, drugs, and insecticides; sulfur compounds also are used to leach ores and recover metals, vulcanize rubber, and condition soils. The physical properties of elemental sulfur, including its low thermal conductivity, high strength, and resistance to acids, suggest potential uses as a versatile construction material (Vroom, 1971). Sulfur should be applied to soils in far greater quantities in many parts of the world to balance chronic sulfur deficiencies.

Sulfuric acid can be replaced by other common acids in many processes, but its low price makes large-scale substitution unlikely.

The United States has an adequate reserve of low-cost sulfur minerals and compounds and large to great resources of moderate- to high-cost sulfur-bearing compounds. In recent years, production, at about 9 million long tons, has exceeded consumption, the balance accumulating in producers stocks. Since World War II, the amount of sulfur rescovered from natural gas and petroleum has been increasing steadily, and present efforts to maintain cleaner air will result in even greater recovery of sulfur from all sources.

EXPLOITATION

It is anticipated that U.S. consumption of sulfur will grow at a rate of 4–5 percent per year, reaching perhaps 30 million tons annually by the year 2000, or about three times the present rate (Hazleton, 1970; Lewis, 1970).

The earliest demand for sulfur in the United States was met by imports of pyrite for acid manufacture and of Sicilian sulfur for nonacid uses. Shortly after 1900, Frasch mining of caprock sulfur deposits became commercially successful; and in the following years, plants also were constructed to recover sulfuric acid from pyrite deposits and base-metal ores. The United States became self-sufficient in sulfur supply during World War I. Between World War I and World War II, most domestic sulfuric-acid plants were converted to use elemental sulfur as primary feed. Following World War II, sulfur was recovered in increasingly larger amounts from sour natural gas and from petroleum. Currently, base-metals smelters are installing units to recover larger amounts of sulfuric acid from flue gases. (See figs. 67 and 68.)

The United States was the major exporter of elemental sulfur to the free world from World War I until the 1950's, when new sources were developed elsewhere: caprock deposits in Mexico (1954), elemental sulfur recovered from sour natural gas in France (1958) and in Canada (1960), and sulfur deposits in evaporites in Poland (1968). Since 1960, sulfur or sulfuric acid has been recovered in increasing amounts from new units in oil refineries in all parts of the world. The United States consequently lost its position as the sole exporter of elemental

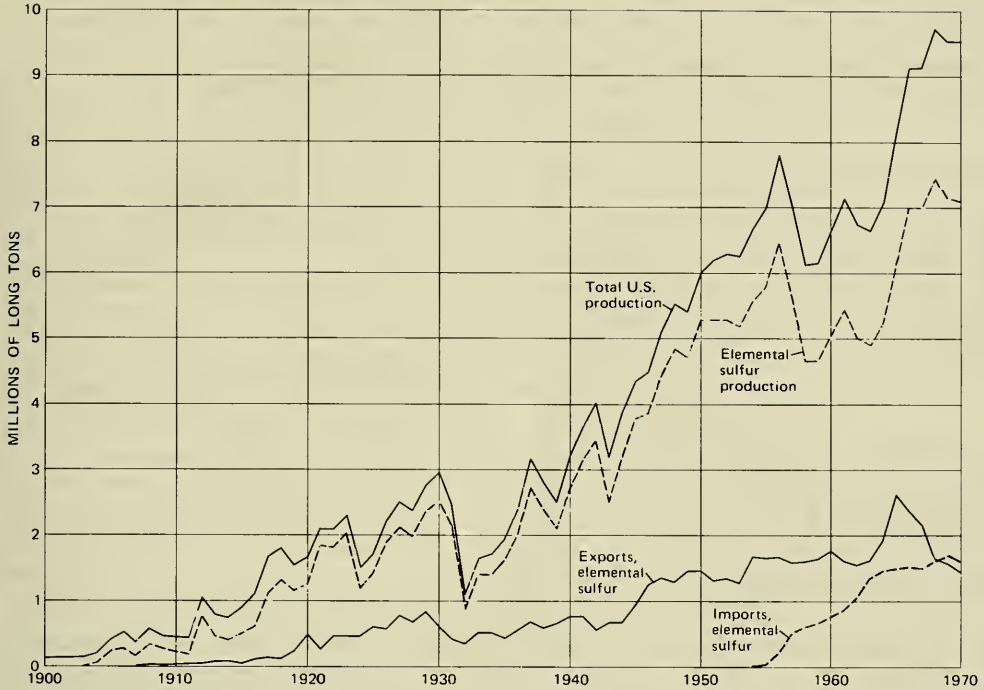

FIGURE 67.—Total sulfur production and production, imports, and exports of elemental sulfur of the United States, 1900–70. Data from U.S. Bureau of Mines.

sulfur and faced increasing competition for its domestic markets from Mexican and Canadian suppliers. By 1968, U.S. exports and imports were about in balance.

The present excess of free-world productive capacity probably will be balanced in about a decade by the steady rise in the demand for sulfur. During this period, however, competition for markets will be intense and sulfur prices will be low. After a balance is achieved, sulfur will be recovered in larger amounts from sources now classed as subeconomic, including perhaps those in coal, gypsum, tar sands, and oil shale.

GEOLOGIC ENVIRONMENT

GEOCHEMISTRY

The average sulfur content of igneous rocks is 520 ppm (parts per million), 13th in order of abundance among all elements. In molten rock, sulfur occurs as the sulfide ion and combines most readily with metallic ions, but it also combines with available hydrogen or oxygen. Sedimentary rocks contain larger amounts of sulfur: sandstone averages 2,000 ppm, shale 2,600 ppm, and limestone 1,100 ppm. In the presence of abundant oxygen, the sulfide ion is oxidized to the sulfate ion, in which form it is contained in the hydrosphere. Sulfur is necessary in trace amounts to all plant and animal life and is constantly being absorbed and released during biologic cycles. Sulfur thus circulates in both inorganic and organic cycles and is both ubiquitous and mobile in all parts of the lithosphere, hydrosphere, atmosphere, and biosphere (Rankama and Sahama, 1950).

THE INORGANIC CYCLE

Sulfur is brought into the earth's crust by molten rock rising from the mantle and combines near the surface with iron and other metallic elements to form the common sulfide minerals or, if oxygen is available, to form sulfates. Where molten rock reaches the surface to erupt volcanically, its sulfur

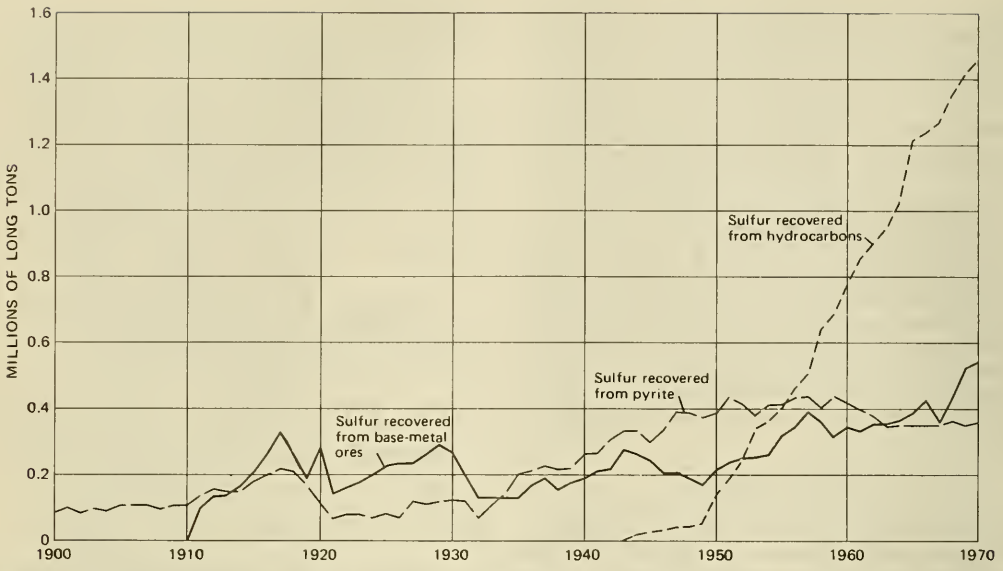

FIGURE 68.—Production of sulfur contained in pyrites, recovered from petroleum and natural gas, and recovered from base-metal ores, United States, 1900–70. Data from U.S. Bureau of Mines.

may (1) combine with hydrogen and be expelled into the atmosphere as hydrogen sulfide gas, (2) combine with oxygen and be expelled as sulfur dioxide gas (the two gases can react and produce elemental sulfur), or (3) combine with metals and form metallic sulfides.

Exposure to atmospheric oxygen breaks down most sulfide minerals to relatively soluble sulfate minerals. Ground and surface waters leach the sulfate minerals and carry their salts to the sea, where the sulfate ion has accumulated in a concentration of 2,650 ppm.

Where restricted arms of the sea spread over continents during periods of aridity, sea water evaporates and becomes increasingly saline, resulting in successive precipitation of calcium carbonate as limestone, calcium sulfate as gypsum, and sodium chloride as common salt. Owing to seasonal and longer range climatic variations, alternating layers of the different evaporites may precipitate. Vast amounts of calcium sulfate as gypsum have been withdrawn from the sea in the course of geologic times (Borchert and Muir, 1964).

THE ORGANIC CYCLE

Sulfur is an essential constituent of certain proteins and fats needed by plants and animals; plants utilize it as sulfate ions from soils, ground water, or sea water. Animals obtain their sulfur from water or by consuming plants or other animals. Upon death and decay, the reduced sulfur is released; on land it enters soils or humic compounds or is emitted into the atmosphere; in seas, it reenters the sea water. The cycle is balanced in the sea, but on the land, sulfur is lost both to the atmosphere and to the sea through the leaching of soil and humins by surface waters.

Bacteria use sulfur compounds in metabolism; some bacteria reduce sulfates, others oxidize sulfides either to sulfates or to elemental sulfur, and still others oxidize elemental sulfur (Davis, 1967). In aerated environments the bacterial sulfur cycle tends to be complete and balanced, but in anaerobic environments the reactions result in only reduction of sulfate ions. The reduction of sulfate is accomplished largely by one species, *Desulfovibrio desulfricans*, an anaerobe found in stagnant marsh waters, tidal flats, oxygen-deficient bottom waters of seas and oceans and in ground water, oil field brines, and petroleum, to depths as great as 5,000 feet below land surfaces. This anaerobe is limited to environments having temperatures less than 165°F.

Desulfovibrio uses dead organic matter, be it

plant, wood, or animal, and both liquid and gaseous hydrocarbons as a source of carbon and hydrogen; at the same time it uses sulfate ions to provide it with oxygen and sulfur. It expels waste carbon dioxide and hydrogen sulfide. It thus converts sulfate waters to carbonate waters and should calcium be available a biogenic variety of limestone may be generated. The hydrogen sulfide can leak into the atmosphere, be retained in rocks at depth, combine with organic material to form organic sulfur molecules, or combine with available metallic ions to form sulfide minerals.

The activities of sulfate-reducing bacteria are probably responsible for most of the iron sulfide minerals in sedimentary rocks of all ages. They probably generated most of the sulfur compounds in petroleum, asphalt, kerogen, and coal, and the hydrogen sulfide contained in sour natural gas (Thode and Monster, 1965). The tonnage of sulfur in the world's beds of gypsum and anhydrite may be exceeded by the total tonnage of sulfur in other sedimentary rocks and fossil fuels. The hydrogen sulfide now being generated by sulfate reducers provides a major source of the sulfur compounds emitted into the atmosphere.

Biogenic hydrogen sulfide also has formed several types of ore deposits. It has been suggested that bacteria generated the hydrogen sulfide that reduced soluble salts and precipitated minable concentrations of uranium. Where these bacteria had a source of hydrocarbons and ample anhydrite rock, they created masses of biogenic limestone impregnated with elemental sulfur, which form the principal elemental sulfur deposits of the world.

ATMOSPHERIC CIRCULATION

Sulfur compounds are constantly circulating in lithosphere, the biosphere, the atmosphere, and the hydrosphere. Some 550 million tons of sulfur compounds, calculated as sulfate-ion equivalent, are thought to be emitted into the atmosphere and returned to the earth's surface annually (Kellogg and others, 1972). A comparable tonnage of dissolved sulfate is carried annually by the world's rivers to the oceans.

More than half the sulfur emitted into the atmosphere results from biologic decay, and about one-quarter each is attributed to windblown sea salt and to manmade pollution; only some 2 million tons of sulfate-ion equivalent is attributed to volcanic activity. About 60 percent of the total emission, some 330 million tons, is thought to fall back on the world's landmasses. Atmospheric fallout of sulfur compounds replenishes the sulfur supply needed by plants, but it settles unevenly on landmasses. The available statistics also indicate that substantially more sulfur is being carried by streams and rivers to the seas than is being replenished by atmospheric fallout. Soils in many parts of the world thus are being depleted of the sulfur needed to sustain optimum plant growth.

DEPOSITS AND RECOVERABLE ACCUMULATIONS

INORGANIC SULFUR

Excluding the very small tonnage of elemental sulfur extracted from volcanic deposits and an even smaller tonnage extracted for only a brief period from one gypsum deposit, sulfur in deposits of inorganic origin has been recovered in the United States only as a byproduct or a coproduct of the mining and smelting of the sulfide ores of metallic minerals.

VOLCANIC DEPOSITS

Gases and acids escaping from volcanoes convert silicate minerals of lava and ash to clay, silica, and sulfate minerals. Any reaction between escaping hydrogen sulfide and sulfur dioxide produces elemental sulfur, which is deposited as replacements, impregnations, and vein fillings in such altered material. The resulting sulfur-bearing masses are apt to be irregular in size, shape, and grade. The gangue of altered material must be removed, a relatively costly process, so volcanic sulfur is mined in the United States only when the price of sulfur is high.

Pyrite is generated in volcanic vents by a reaction between hydrogen sulfide and iron. Pyrite may be deposited as disseminations or masses in the altered rock and is minable as a sulfur ore in some parts of the world.

Elemental sulfur also is deposited by hot springs, probably the result of near-surface oxidation of hydrogen sulfide emissions. Gangue consists of altered rock and various minerals precipitated by the springs. Most such deposits are low in grade and have rarely been mined.

Volcanic deposits of sulfur are known in California, western Nevada, and Alaska, and hot-spring deposits occur in various Western States.

HYDROTHERMAL SULFIDE DEPOSITS

When molten rocks crystallize at depth, some of their metals and sulfur are concentrated in hydrothermal solutions and ultimately deposited as disseminations, masses, or veins either within or outside the cooling masses, thus forming sulfide ore deposits of copper, molybdenum, lead, zinc, and other metals. During the smelting of such ores, the sulfide is converted into gaseous sulfur dioxide which, with

appropriate smelting techniques and installations, can be recovered and converted to sulfuric acid or, at a greater cost, to elemental sulfur. Sulfide ore deposits thus are actual or potential sources of recoverable sulfur compounds.

The geology of metallic-sulfide deposits is described in other chapters of this volume, but mention should be made here of masses of pyrite and pyrrhotite deposited from hydrothermal solutions, generally containing only small amounts of metals other than iron. In some parts of the world, such iron sulfides are roasted to provide sulfur dioxide used in sulfuric-acid manufacture; iron and any accompanying metals may be recovered as coproducts. Only one such mass of pyrite in the United States (Ducktown, Tenn.) is exploited as a large supplier of sulfuric acid, but it contains sufficient values of copper and other metals to be classed as a base-metal deposit (Kinkel and others, 1968). The resources of sulfur contained in other masses of pyrite that have little or no base metals occur mainly in Eastern States, less commonly in Western States, and in Alaska (Espenshade and Broedel, 1952). The deposits are relatively large and probably will be utilized after lower cost sources of sulfur are exhausted.

GYPSUM

Gypsum deposited during the evaporation of sea water forms beds that may contain layers of calcite or dolomite, and may contain beds of clay, silt, or sand derived from surrounding arid lands. When buried, gypsum ($CaSO_4 \cdot 2H_2O$) loses its water of crystallization and is converted to anhydrite ($CaSO_4$). In contact with ground water, anhydrite reconverts to gypsum. The transformation has been noted at depths ranging from several tens of feet to about 1,000 feet.

Gypsum and anhydrite are widespread in the United States. (See chapter on "Evaporites and Brines".) Reserves and resources are vast, but it is not known what fraction is sufficiently pure to be used as a raw material for production of sulfuric acid or elemental sulfur. The one plant designed to produce elemental sulfur from gypsum, near Van Horn, Tex., was supplied from a large reserve of very pure gypsum, virtually free of interbedded carbonates and clastic material. The explored block, still nearly intact, is in the upper part of the Castile Gypsum, a unit of Permian age in the Delaware Basin of west Texas (Jones, 1954; and Adams, 1969).

The cost of converting gypsum or anhydrite to sulfuric acid or elemental sulfur is well above the cost of mining elemental sulfur or recovering sulfur from hydrocarbons or metallic ores. It can nonetheless be a future source of our sulfur supply after lower cost raw materials now available are mined out.

ORGANIC SULFUR

The conversion of sulfate ions to sulfide ions by anaerobic bacteria produced the chief sources of sulfur now minable at lowest cost, particularly the elemental sulfur deposits in accumulations of evaporite, the organic sulfur contained in petroleum, and the hydrogen sulfide associated with sour natural gas. Even greater tonnages of sulfur compounds of the same derivation are locked in coal, oil shale, and tar sands (Theobald and others, 1972; and Duncan and Swanson, 1965).

ELEMENTAL SULFUR DEPOSITS

Bacterial attack on anhydrite produces lenses of limestone impregnated with elemental sulfur. Such deposits are formed in two stages: the first resulting in the formation of masses of porous, vuggy medium-grained gray limestone and the second in the formation of coarsely crystalline white calcite and elemental sulfur deposited within the pores and openings in the limestone (Hanna, 1934). Very small amounts of selenite, barite, and celestite may be deposited later. The reactions theoretically produce 1 ton of sulfur for every 3 tons of calcite, or an ore containing nearly 25 percent sulfur, but no limestone lenses contain this theoretical amount because hydrogen sulfide is so highly mobile and tends to escape from its zone of generation. The grade, porosity, and permeability of deposits differ over a substantial range.

Elemental sulfur deposits of this type are associated with anhydrite caprocks of probable Cenozoic age overlying salt diapirs in the gulf coast and also occur in widespread sequences of anhydrite of Permian age in west Texas. In both areas, deposits range from small pockets containing several thousand tons to large accumulations containing tens of millions of tons of sulfur. The Boling Dome deposit, Texas, the largest in the gulf coast, underlies an area of 1,500 acres and has yielded 70 million tons of sulfur to date; the Culbertson property deposit, the largest in west Texas, is said to contain about 80 million tons of sulfur underlying an area of 1,200 acres. The depth of minable sulfur deposits has ranged from 400 to 3,200 feet. Some 30 deposits are known in the gulf coast, many of them mined out, and perhaps 10 have been found as the result of recent exploration in west Texas (Hawkins and Jirik, 1966; Ellison, 1971; and Zimmerman and Thomas, 1969). Twelve such deposits currently being mined supply about 75 percent of the sulfur produced in the United States.

A specific sequence of geologic events must take place, and specific geologic conditions must be met before sulfur deposits can form; should any one element be missing, sulfur mineralization will not occur. Both in the gulf coast and in west Texas, the basic conditions needed for sulfur mineralization are (1) solution of evaporite minerals, forming porous ground, (2) migration of petroleum into the prepared ground, (3) generation and retention of hydrogen sulfide gas within the formation, and (4) oxidation of the hydrogen sulfide to elemental sulfur. The required geologic steps differ between the gulf coast and west Texas, as described in the following paragraphs.

GULF COAST

Preparation of the ground in the gulf coast entailed formation of lenses of anyhdrite over the upper surfaces of salt diapirs, which consist of impure rock salt containing only several percent anhydrite. Ground water dissolved the salt at the upper surfaces of the diapiric masses, permitting residual accmumlation and subsequent lithification of the less soluble anhydrite. Anhydrite accumulated in appreciable thicknesses only where aquifers intersected the apexes of salt diapirs and where the rate of upward flow of rock salt was equalled by the rate of salt solution, providing stable surfaces upon which the anhydrite could accumulate. Conditions favoring caprock development differed widely, inasmuch as anhydrite lenses range in thickness from a few feet to more than 1,000 feet; more than one-third of the 190 diapirs in the gulf coast are overlain by less than 200 feet of anhydrite, thicknesses inadequate to permit formation of sulfur deposits of commercial size (Taylor, 1938; Goldman, 1952; Murray, 1961; Halbouty, 1967; Bodenlos, 1970).

During their intrusion, salt masses dragged surrounding strata upward and produced structures favoring migration of hydrocarbons toward the diapirs. Hydrocarbons entered most, but not all, caprocks partly because oil sands do not underlie the entire diapiric province, and partly because petroleum was too tightly held in peripheral traps to have escaped in quantity. As a result, biogenic limestone produced by bacterial attack overlies anhydrite as lenses ranging from a few to hundreds of feet in thickness.

Hydrogen sulfide was retained and oxidized to elemental sulfur only where host caprocks were overlain by thick beds of impermeable clay or mudstone. Caprocks barren of sulfur are overlain either by thin beds of clay or directly by porous sandstone, which permitted hydrogen sulfide to escape.

The incidence of sulfur deposits in the gulf coast indicates how infrequently all steps leading to their generation are met. Of the 190 salt diapirs in the gulf coast, the caprocks of only 18 contained ore bodies yielding more than 1 million tons of sulfur; another three or bodies opened more recently undoubtedly contain ore bodies of substantial size.

Although the structures produced by intrusion of salt diapirs favor migration of ground water and hydrocarbons toward the salt masses, the critical factors needed to produce sulfur deposits seem to be stratigraphic—permeable strata are needed up to the apexes of diapers to permit the flow of fluids, whereas impermeable strata are needed above caprocks to retain hydrogen sulfide. It seems unlikely that sulfur deposits can form in stratigraphic sequences uniformly coarse grained or uniformly fine grained and impermeable.

WEST TEXAS

The sulfur deposits in west Texas occur in thick extensive units of bedded anhydrite of evaporite origin that underlie the entire Delaware Basin and adjacent platforms. As bedded anhydrite is one of the least permeable of rocks, greatly inhibiting movement of ground water and hydrocarbons, ground was prepared for sulfur mineralization by a sequence of events differing from that in the gulf coast. Evidently all deposits in west Texas were formed in lenses or chimneys of anhydrite collapse breccia, so it seems probable that ground water moved upward along joints or faults from underlying aquifers and dissolved anhydrite at the base of the evaporite units. This solution process produced an underground, cavernous karst system, into which overlying anhydrite collapsed. Hydrocarbons ascending along the same fissures from underlying oil sands then penetrated the breccias, and the broken anhydrite was altered through bacterial activity to a fine- to medium-grained gray limestone. Thereafter, white calcite and elemental sulfur were deposited in the breccia voids and in the pores of the gray limestone (Davis and Kirkland, 1970; Hinds and Cunningham, 1970; McNeal and Hemenway, 1972).

Some mineralized breccia masses are confined to the lowermost parts of the anhydrite units, but others extend as chimneys completely through them, impinging against overlying carbonate or clastic beds. Chimneys breaking through anhydrite units exposed at the surface produced swallow holes that diverted surface drainage, and the voids in the breccia became clogged with very fine to coarse-grained alluvium. In the west Texas deposits, the seals

needed to retain hydrogen sulfide in breccia masses until the gas was oxidized to elemental sulfur differ from deposit to deposit, consisting either of overlying anhydrite, overlying impervious strata, or of alluvial clay and silt within the breccia masses. Notwithstanding, many limestone breccia masses are barren of sulfur, indicating that they were not sealed against loss of hydrogen sulfide gas.

The location of west Texas sulfur deposits seems to have been controlled largely by structure. Deposits lying near the southwest side of the Central Basin Platform occur in anticlinal highs, whereas those in the western part of the Delaware Basin seem to occur along or near lineaments that may represent faults of small displacement. Notwithstanding, no clear-cut controls have been found that satisfactorily explain the location of the huge deposit in Culbertson County.

SULFUR-FORMING REACTIONS

Regarding the chemical reactions that produced the deposits, it is generally agreed that anaerobic bacteria reduced the sulfate ions of anhydrite. Views differ, however, on the manner in which hydrogen sulfide is oxidized to elemental sulfur. Three possible reactions have been proposed: (1) inorganic reaction between the gas and calcium sulfate molecules: (2) oxidation of the gas by free oxygen carried in ground water; and (3) oxidation of the gas by sulfide-oxidizing bacteria (Feely and Kulp, 1957; Davis and others, 1970; and Ivanov, 1968). With particular regard to sulfur deposits in the gulf coast, the second proposal seems to be unfeasible because ground waters there are nearly devoid of free oxygen; the required volumes of water would flush out the accumulated hydrogen sulfide before oxidizing any appreciable amount of that gas. Nor does it seem likely that aerobic, sulfur-oxidizing bacteria could coexist with anaerobic bacteria in the oxygen-deficient, hydrogen sulfide-saturated solutions contained in cap rock. It thus seems that an inorganic reaction between hydrogen sulfide and calcium sulfate would be the most likely to occur. Although this reaction can proceed thermodynamically only at slow rates, it produces both sulfur and a small amount of calcite, which in fact are deposited together during the second stage of mineralization.

SULFUR ACCUMULATIONS IN HYDROCARBONS

Bacterial attack upon sulfate ions in stagnant waters produces hydrogen sulfide that can combine with organic matter in the associated sediments; the sulfur-bearing molecules can then be incorporated into hydrocarbons formed from such parent material. Most crude oils, tar sands, asphalts, and organic-rich shales therefore contain sulfur even if only in low concentrations. The sulfur content of petroleum can range from traces to as much as 14 percent, although crude oil containing more than 5 percent sulfur is relatively uncommon. Two-thirds of the petroleum produced in the United States contains less than 1 percent sulfur, and only about one-tenth contains more than 2 percent sulfur (McKinney and Shelton, 1967).

The geologic conditions leading to the wide range of sulfur in hydrocarbons are not well known. It can be assumed that coarser grained sediments will retain less hydrogen sulfide than finer grained sediments. The concentration of sulfate ions available for reduction also can differ, being lowest in seas near the mouths of large rivers and highest in basins undergoing evaporation. Still another variable is the iron content of source beds and connate waters, which will determine how much hydrogen sulfide will be withdrawn from the system as iron sulfide. All these variables probably played a part in determining how much sulfur was incorporated into the parent material of any given crude oil.

As petroleum matured and migrated, heavier sulfur-bearing molecules could have been filtered out and hydrogen sulfide perhaps was generated as constituent molecules were reconstituted, both mechanisms leading to a reduction of sulfur content of the liquid fraction. Variations in sulfur content also have been noted within given oil pools, but in the aggregate all such changes can only modify the amount of sulfur originally accumulating with the parent organic material.

The sulfur in tar sands is probably higher than the original concentration if it can be assumed that liquid and gaseous fractions containing less sulfur migrated elsewhere, whereas the sulfur in shales rich in organic matter must be that generated in place.

Theories of origin for hydrogen sulfide in natural gas are diverse. Hydrogen sulfide and methane can be generated simultaneously in fresh-water swamps, for example, and perhaps both gases were distilled together as sulfur-bearing petroleum underwent chemical reconstitution at high pressures and temperatures. Sulfate ground water coming in contact with petroleum activates anaerobic bacteria and results in generation of hydrogen sulfide, and the same reactions can take place where petroleum is trapped under beds of anhydrite. Although most sour natural gas contains only a few percent hydrogen sulfide, some contains more than 80 percent of

that gas, undoubtedly the result of long-extended contact between petroleum and anhydrite.

SULFUR ACCUMULATIONS IN COAL

Reactions already described also occurred in swamps sufficiently stagnant to preserve as peat the organic matter contained in plants and trees, at the original sites of our present lignite and coal beds. Anaeorbic bacteria reduced any available sulfate ions and emitted hydrogen sulfide, which combined with organic material or was deposited as pyrite. Sulfur from this source augmented the traces of sulfur originally contained in the plant matter. In coal low in sulfur, the element largely is in organic molecules, whereas in coal high in sulfur, the element largely is in pyrite or marcasite. U.S. coals contain sulfur that ranges in amount from a trace to 7 percent (DeCarlo and others, 1966; Walker and Hartner, 1966).

Most swamps in which coal formed in the United States lay close to sea level, so the slightest changes in levels produced widespread marine transgressions or regressions, either bringing in an abundant supply of sulfate ions in sea water or bringing in fresh waters from land. Williams and Keith (1963) suggested that swamps transgressed by seas resulted in coals higher in sulfur than those which lay in areas of subsequent marine regression. Because sea water contains very little iron, only 2–20 parts per billion, marine transgression in itself cannot produce coal with high pyrite content; sources of iron from hinterlands behind coal-forming swamps also seem to be needed. It appears to be more than coincidental that most of our high-sulfur coals, those of Pennsylvanian age in the Illinois and midcontinent fields, were closest geographically to the iron-formations and iron deposits of Wisconsin, Michigan, and Minnesota. Conversely, coals lowest in sulfur content, those in our western fields, seem to have been deposited in environments in which seas were excluded by offshore bars and concurrently were at some distance from any terrane high in iron.

RESOURCES

The world's total resources of sulfur are vast, but only a fraction is minable or recoverable now at competitive prices (Hazleton, 1970; Ambrose, 1965; Lewis, 1970; British Sulphur Corp., 1966; President's Materials Policy Comm., 1952; Little, 1966). The previous estimates of the world's sulfur resources have differed widely for many reasons, including the factors discussed in the previous section on the geology of the deposits, and because of the lack of data on ore deposits in the remoter parts of the world.

Estimates of identified, hypothetical, and speculative resources of sulfur in various types of deposits in the United States, Canada, and Mexico are compiled in tables 126 and 127. The compilation of the data for the United States is more detailed than that for Canada and Mexico. Only the more economically important accumulations of sulfur elsewhere in the world are cited in the following discussion.

THE UNITED STATES

The identified sulfur resources of the United States are divided into three categories: (1) recoverable, those accumulations that can be mined or recovered at prices less than $25 per long ton,

TABLE 126.—*Identified*[1], *hypothetical*[2], *and speculative*[3] *sulfur resources of the United States*

[In millions of long tons; +, some resources, but amount not estimated]

Source	Identified resources				Hypothetical resources	Speculative resources	Total
	Recoverable	Paramarginal	Submarginal	Subtotal			
1. Elemental sulfur deposits in evaporites	150	40	10	200	100	150	450
2. Hydrogen sulfide in sour natural gas	10	5	----	15	[4] 185	---	200
3. Organic sulfur in petroleum	10	25	220	255	[4] 1,000	---	1,255
4. Pyrite deposits	10	30	60	100	20	20	140
5. Elemental sulfur in volcanic rocks	---	10	20	30	+	+	30
6. Sulfur contained in metallic sulfides	20	40	40	100	100	200	400
7. Gypsum	---	150	7,050	7,200	1,800	---	9,000
8. Organic sulfur in tar sands	---	---	10	10	----	---	10
9. Organic sulfur and pyrites in coal	---	---	21,400	21,400	[4] 19,600	---	41,000
10. Organic sulfur and pyrites in oil shale and shale rich in organic matter	---	+	+	+	+	---	81,000
Total	200	300	28,810	29,310	22,805	370	133,485

[1] Identified resources: Specific, identified mineral deposits that may or may not be evaluated as to extent and grade, and whose contained minerals may or may not be profitably recoverable with existing technology and economic conditions.
[2] Hypothetical resources: Undiscovered mineral deposits, whether of recoverable or subeconomic grade, that are geologically predictable as existing in known districts.
[3] Speculative resources: Undiscovered mineral deposits, whether of recoverable or subeconomic grade, that may exist in unknown districts or in unrecognized or unconventional form.
[4] Includes some speculative resources.

TABLE 127.—*Sulfur resources of Canada and Mexico*

[In millions of long tons]

Source	Canada			Mexico		
	Identified resources [1]	Hypothetical [2] and speculative [3] resources	Total	Identified resources [1]	Hypothetical [2] and speculative [3] resources	Total
1. Elemental sulfur deposits in evaporites	---	---	---	80	50	130
2. Hydrogen sulfide in sour natural gas	140	185	325	---	---	---
3. Organic sulfur in petroleum	5	([4])	5	5	([4])	5
4. Pyrite deposits	[5] 25	25	50	[5] 25	25	50
5. Elemental sulfur in volcanic rocks	---	---	---	5	---	5
6. Sulfur contained in metallic sulfides	35	100	135	25	40	65
7. Gypsum	([6])	([6])	---	([6])	([6])	---
8. Organic sulfur in tar sands	40	1,800	1,840	---	---	---
9. Organic sulfur and pyrites in coal	([4])	([6])	---	([4])	([4])	---
10. Organic sulfur in oil shale and shale rich in organic matter	([6])	([6])	---	---	---	---
Total	245	2,110	2,355	140	115	255

[1] Identified resources: Specific, identified mineral deposits that may or may not be evaluated as to extent and grade, and whose contained minerals may or may not be profitably recoverable with existing technology and economic conditions.
[2] Hypothetical resources: Undiscovered mineral deposits, whether of recoverable or subeconomic grade, that are geologically predictable as existing in known districts.
[3] Speculative resources: Undiscovered mineral deposits, whether of recoverable or subeconomic grade, that may exist in unknown districts or in unrecognized or unconventional form.
[4] Not known; resources probably small.
[5] Including pyrite in base-metal deposits.
[6] Not known; resources probably large.

f.o.b. gulf coast ports; (2) paramarginal, those available at prices between $25 and $35; and (3) submarginal, those estimated to be available at prices higher than $35 per ton. Hypothetical and speculative resources are comparable to those are defined throughout this volume. Comments on each of the principal accumulations follow.

1. Identified resources of elemental sulfur in evaporites cannot be estimated accurately because operating companies do not release reserve data. It is judged, however, that some 200 million tons of sulfur remains in the known deposits, 100 million tons each in the gulf coast and in the west Texas occurrences. Of the total of 200 million tons, some 40 million tons is thought to be minable only when the price of sulfur approaches $35 a ton, and another 10 million tons is thought to be minable only when the price exceeds $35 a ton. Another 100 million tons of sulfur, which may be found in west Texas, is shown in table 126 as part of hypothetical resources.

   In the United States, anhydrite occurs in many petroliferous sedimentary basins, including the Michigan, Williston, Paradox, and Permian basins; anhydrite also occurs at great depths in the gulf coast geosyncline. Elemental sulfur deposits could have formed in all or any of these areas, and one can speculate that at least 100 million tons of sulfur ultimately will be discovered in them.

   The possibilities for further discovery of elemental sulfur deposits in anhydrite caprocks overlying salt diapirs are somewhat more limited because of the diverse geological processes and conditions required in their generation. Salt diapirs are common structures known on all continents and continental shelves in many parts of the world (McKelvey and Wang, 1970), yet only in the gulf coast of the United States and Mexico have deposits of commercial size been found in caprocks. It can be anticipated that several more sulfur deposits, containing perhaps 50 million tons of sulfur, will be found in the offshore extension of the gulf coast belt of the United States.
2. Hydrogen sulfide in natural gas yielded about 30,000 tons of sulfur per trillion cubic feet of produced gas in 1971. Using this ratio, some 15 million tons of sulfur is estimated to remain in the identified resources of natural gas (Theobald and others, 1972). Another 65 million tons may occur in recoverable undiscovered resources, and 120 million tons, in the submarginal undiscovered resources (combined as 185 tons of hypothetical resources in table 126).
3. Each billion barrels of petroleum in the United States reserve contains nearly 1 million tons of sulfur (U.S. Bur. Mines, 1971), a ratio which indicates that some 10 million tons of sulfur is contained in the recoverable petroleum and 245 million tons in the petroleum that can only be extracted with difficulty. Another 1 billion tons of sulfur may occur in the undiscovered petroleum resoruces, of which 20 percent is a recoverable resource and 80 percent is a subeconomic

resource. The preceding calculations were restricted to the petroleum in the conterminous United States, inasmuch as petroleum under the continental shelves and in Alaska is so low in sulfur that a resource in such oil should not be postulated.

4. Of the 100 million tons of sulfur contained in the identified resource of pyrite, 10 million tons arbitrarily is assigned to the recoverable fraction, and the balance, to the subeconomic resources. The President's Materials Policy Commission (1952) considered that some 30 million tons of sulfur, contained as pyritic gangue in base-metal ores, constitutes a resource. Although much of that pyrite will be rejected with tailings in nonrecoverable form, it is judged that 20 million tons of this sulfur eventually could be recovered, and this amount is included with the submarginal resources of pyrite deposits shown in table 126. Another 40 million tons may occur in extensions of known districts and in areas as yet unexplored.
5. The 30 million tons of subeconomic resources of sulfur in volcanic rocks cited for many years is probably still a reasonable estimate. Hypothetical and speculative resources are judged to be very small.
6. Resources of sulfur contained in sulfide ores of base metals are calculated from estimates presented in other chapters of this volume. A nominal recoverable resource of 20 million tons is predicated on recovery efforts prior to present statutory requirements for cleaner air. Much of the subeconomic identified resources, some 80 million tons, will be recovered regardless of cost because of antipollution regulations.
7. Gypsum resources are nearly 50 billion tons, the sulfur content of which constitutes an identified resource of about 7 billion tons, and a hypothetical resource of nearly 2 billion tons. Of this amount, 150 million tons of very pure gypsum has been blocked out as raw material for sulfur production. At present this constitutes a paramarginal resource. Huge anhydrite resources, many times greater than gypsum resources, are not included in the accompanying tabulation.
8. Tar sands are said to contain an identified submarginal resource of 10 million tons of sulfur.
9. The aggregate tonnage of sulfur contained in coal is enormous. Resources of all classes are estimated to be 41 billion tons, but none is recoverable at present prices of sulfur. In table 126, the hypothetical sulfur resource in coal is predicated on undiscovered coal lying at less than 6,000 feet depth.
10. Shales rich in organic matter, eventually exploitable as sources of liquid or gaseous hydrocarbons, contain at least 1 billion tons of sulfur in the oil shale of the northern Rocky Mountains, and 80 billion tons in the black shales of Devonian and Mississippian age in the Eastern and Central United States. The entire resource is subeconomic; no attempt is made here to differentiate between identified and hypothetical resources.

RECOVERY

Recovery of sulfur from resources depends upon the state of the technology, upon the cost of extraction, and now also upon statutory requirements limiting sulfur emissions into the atmosphere. The resource data already presented must thus be qualified as follows:

Frasch mining recovers 75–92 percent of the sulfur contained in the ground, depending on the technological efficiency of the operating companies and on the geological characteristics of given ore bodies. Recovery of sulfur from natural gas exceeds 95 percent of the contained hydrogen sulfide, but only about 80 percent of the natural gas is recoverable from the ground. Recovery of sulfur from petroleum has been averaging 15–20 percent, and less than half the petroleum in the ground is recoverable under current technology. Recovery of the sulfur contained in pyrites is relatively high and that of sulfur in volcanic deposits reasonably high, both probably greater than 75 percent. Recovery of the sulfur contained in base-metal ores has been relatively low in the past, but should increase markedly in the coming years. Experience in the extraction of sulfur from gypsum, tar sands, and oil shale is yet too limited to indicate how efficient recovery will be.

Little sulfur is recovered from petroleum in the United States. The low sulfur content of most U.S. oils has made extraction of sulfur during petroleum refining seem neither necessary nor economically important. The same is true with other deposits of hydrocarbons and with low-sulfur coal. About 30 percent of the bituminous coal of the United States contains less than 1 percent sulfur.

CANADA AND MEXICO

Canada and Mexico are among the leading producers of elemental sulfur. Canada recovers the element from hydrogen sulfide in natural gas and Mexico from caprock deposits. The sulfur in Canadian natural gas is an indicated resource of 140

million tons (Cote, 1971), that in Mexican caprocks an indicated resource of 80 million tons (table 127). Both countries also are well endowed with deposits of base-metal sulfides and with bedded gypsum from which sulfur can be recovered. Canada also has vast resources of tar sands, whose bitumens contain an average of 4.5 percent by weight of sulfur, which amounts to a multibillion ton resource of sulfur. The 40 million tons shown in table 127 as the identified sulfur resources of the Canadian tar sands is that sulfur currently available for extraction in existing processing facilities. Some petroleum in southeastern Mexico contains enough sulfur to warrant its recovery during refining.

The hypothetical and speculative resource data shown in table 127 summarize those resources whose discovery can be reasonably expected in known mineral districts and petroliferous areas and in untested regions. The postulated resource of 1,800 million tons of sulfur in tar sands should perhaps be listed partly as a subeconomic identified resource. Speculative resources of sulfur in Mexico include an estimated 50 million tons of elemental sulfur in caprocks on salt diapirs in the southeastern part of the country. These deposits will be similar to those known in the gulf coast of the United States.

OTHER COUNTRIES

Sulfur resources outside of North America also are vast; apparent reserves totaling nearly 2 billion tons have been estimated recently by Lewis (1970). Only the most notable concentrations are cited in the following brief discussion.

1. Elemental sulfur deposits containing an identified resource of 100 million tons occur in bedded anhydrite of Miocene age in southern Poland. The belt of anhydrite extends into the U.S.S.R., where other sulfur deposits probably occur. Although the belt in the U.S.S.R. is not now petroliferous, hydrocarbons in the past evidently leaked upward into it at many places. The greatest potential for discovery of elemental sulfur outside the United States is in the Middle East, where the world's greatest accumulations of hydrocarbons coincide with extensive anhydrite beds. In Iraq, one deposit of elemental sulfur in anhydrite of Miocene age contains an identified resource of 200 million tons of sulfur. Most of the readily available sulfur in the bedded evaporites of Sicily has been mined.

   The salt diapirs of northern Europe and of the Middle East seem to be barren of sulfur deposits. Possibilities exist for caprock sulfur mineralization in the northern Caspian area and northern Siberia in the U.S.S.R., perhaps over the diapirs lying under the Persian Gulf and under the North Sea, and over those diapers in the Canadian Arctic Islands. Neither the Canadian nor the North Sea areas would favor low-cost exploitation of any sulfur discovered.
2. Hydrogen sulfide amenable to extraction from sour natural gas is moderately abundant in France and in eastern Europe, but the largest resource of such sulfur is in the Middle East, where about 500 million tons occurs in the very large natural gas resources.
3. The petroleum of the Middle East perhaps contains about 300 million tons of sulfur, and that of Venezuela at least 30 million tons.
4. Resources of sulfur in pyrite deposits are large and widespread. At least 500 million tons of sulfur occurs in Spanish deposits and perhaps an equivalent amount may occur in the pyrite deposits elsewhere in Europe. Such resources also are abundant in South America, the Middle East, Africa, and Australia.
5. Elemental sulfur in volcanic rocks in the circum-Pacific belt provides a resource totaling 100–200 million tons. Japan and Chile have most of these resources. Pyrite in volcanic deposits in this region also constitutes a large resource.
6. Outside North America, at least 200 millon tons of sulfur occur in the known base-metal sulfide deposits scattered on all other continents. Pyrite included in these ores also constitutes an appreciable resource of sulfur.
7. Anhydrite and gypsum underlie large areas on every continent (McKelvey and Wang, 1970) and form an almost unlimited resource of sulfur.
8. Tar sands are abundant in Venezuela, but the tonnage of their sulfur never has been calculated.
9. Extrapolating the average sulfur content of coal in the United States to that in coal outside North America, it would seem that at least 180 billion tons of sulfur occurs in the coal on other continents.
10. Oil shale and shale rich in organic matter seem to contain at least as much sulfur as does coal; therefore, the sulfur resources in such accumulations outside North America could reach several hundred billion tons.

Lastly, sea water contains sulfate ions in low

concentrations but provides a virtually unlimited sulfur resource.

In summary, the world position on sulfur resources is good and will sustain rates of production many times higher than present rates without strain.

PROSPECTING FOR ELEMENTAL SULFUR DEPOSITS

Most caprock sulfur deposits were discovered through wildcat drilling in search for oil, but some were found by either wildcat or systematic drilling in search for sulfur. Geophysical prospecting to date has not been effective in locating sulfur deposits, although it can be used to located caprock of unspecified composition.

It has long been known that on the gulf coast, acid soil, known as sour dirt, occurs over known caprocks; such soil is acidified by leakage of hydrogen sulfide from below. This geochemical evidence was instrumental in locating several caprock oil fields and also provided the first clue to the presence of a sulfur deposit in Boling Dome, Tex. (Haynes, 1942). Acid soil, hydrogen sulfide emissions, and sulfuric acid springs also are known in west Texas but do not necessarily coincide with underlying sulfur deposits. They cannot be infallible geochemical indicators of sulfur deposits simply because they show only that hydrogen sulfide was generated, not that it was retained and oxidized to sulfur at depth.

Regional stratigraphic features in the gulf coast region and local structural features in the Delaware Basin of west Texas could be applied to a greater extent in exploration for sulfur. Particularly on the outer continental shelf, study of stratigraphy could be applied to block out favorable and unfavorable areas for generation and retention of hydrogen sulfide within caprocks. Study of faulting in the Delaware Basin may lead to targets overlooked in previous exploration programs.

PROBLEMS FOR RESEARCH

Geological problems still to be resolved include determination of all the factors leading to the accumulation of sulfur in coal, petroleum, natural gas, and shale rich in organic matter. The various hypotheses advanced to date need to be tested and evaluated over sufficiently broad areas to determine their validity and hence their usefulness in exploring for low-sulfur coal or, if sulfur is being sought, for fossil fuels high in that element.

A related geological problem needing further study is the generation in coal mines of sulfuric acid, a troublesome pollutant in streams traversing coal-mining districts. A fuller understanding of the natural processes involved will lead to better methods of controlling acid generation.

Perhaps more research has been devoted to methods of recovering sulfur or removing it as an unwanted element than to the recovery of any one other mineral commodity. The wide variety of raw materials now yielding sulfur as a byproduct attests to the past successes of these efforts. Research is continuing, nevertheless, to reduce the costs or to increase the efficiency of sulfur recovery processes applying to several of these raw materials. Major research efforts now are being directed to the problem of removing sulfur from coal. Techniques are being studied for removal of pyrite before ignition of the coal, removal of sulfur dioxide from stack gases, with or without the recovery of the sulfur itself, and removal and recovery of sulfur from coal as it is being gasified or liquified. Until these techniques are perfected, much coal must remain in the ground because it contains too much sulfur to meet clean-air requirements.

The present excess sulfur production, particularly in Canada, is stimulating research on new uses that will exploit the unique physical properties of sulfur. The element is remarkably low in thermal and electrical conductivity, completely inert to attack by acids, impervious to water, and it has high strength at normal ambient temperatures; it is easily applied and workable when plasticized or in molten form, and it hardens quickly. It thus promises to be a versatile construction material.

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TALC

By C. Ervin Brown

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ABSTRACT OF CONCLUSIONS

Talc as mined and used industrially is a rock containing a mixture of magnesium-rich silicates and ranging in mineral composition from pure talc to predominant tremolite. Other minerals commonly present in talc rock are serpentine, diopside, anthophyllite, and chlorite and less abundantly the carbonates calcite, dolomite, and magnesite.

Industrial talc is used in the pulverized form as a ceramic base for floor and wall tile; a paint extender; a filler for rubber, paper, plastics, roofing, and many other products; a diluent or carrier for pesticides; and a polishing or dusting agent.

Talc is mined from metamorphosed dolomitic and quartzose sedimentary rocks or from hydrothermally altered ultramafic and mafic rocks. The main producing areas are in the eastern States from New England to Alabama and in the west in California, Nevada, Montana, and Texas.

In 1969 and 1970, total consumption was over a million tons—double that of 20 years ago. The projected demand for the year 2,000 ranges from 2.28 to 3.36 million tons. Resources of talc are large and should be adequate to meet this demand, although deposits meeting the rigid chemical and physical specifications of some consumer industries are relatively scarce. Although all talc mining districts contain known reserves and have a good to excellent potential for the discovery of additional reserves, the great bulk of reserves are in New York and Vermont.

Most industrial areas of the United States are fairly close to a source of industrial talc, except for the industries of the midcontinent. There, shipping charges are a much larger part of the cost of talc because most supplies are shipped from Montana and Texas. Areas of metamorphic rocks in Wisconsin and Michigan could contain talc deposits more favorably located for the midcontinent market.

INTRODUCTION

The purposes of this report are to present a current picture of the resources of industrial talc in the United States and to assess the potential for additional resources. A talc resource study by Chidester, Engel, and Wright (1964) is the latest extensive account giving detailed descriptions of many of the talc deposits in the United States and a discussion of all talc-producing districts. Subsequent studies have been published for deposits in Alabama (Neathery, 1968; Neathery and others, 1967), California (Wright, 1968), and New York (Brown, 1969). Bibliographies of talc in the United States are available in works of Engel and Wright (1960) and Merrill

(1963), and a map locating all talc-mining areas was published by Chidester and Worthington (1962).

MINERALOGY AND PHYSICAL PROPERTIES

Talc is a hydrous magnesium silicate mineral with the theoretical formula $H_2Mg_3(SiO_3)_4$. As used industrially, however, the term "talc" refers to a rock composed mainly of magnesium-rich silicate minerals and having the mineral talc as an important constituent. Mineral content of industrial talc can range from pure talc to predominantly tremolite.

Minerals other than talc that are most commonly present in industrial talcs are serpentine ($H_4Mg_3SiO_9$), chlorite (hydrous Mg-Fe-Al silicate), tremolite ($Ca_2Mg_3H_2(SiO_3)_8$), anthophyllite ($(Mg,Fe)_7(OH)_2Si_8O_{22}$), and diopside ($CaMg(SiO_3)_2$); less commonly present are quartz (SiO_2), calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), and magnesite ($MgCO_3$). Pyrophyllite, an aluminum silicate ($Al_2Si_4O_{10}(OH)_2$) closely related to talc in structure, properties, and uses, is generally lumped with talc and soapstone in production and consumption statistics, but it is not included in this discussion.

The constituents of industrial talc differ considerably in physical and mineralogic properties, consequently, rocks having different mineral proportions vary accordingly in their properties. The mineral talc is extremely soft and slippery, having a hardness of 1 on the Mohs scale; and because of a strong basal cleavage, it is flaky. The associated tremolite and anthophyllite have a hardness of 5 to 6 and when ground produce a fibrous powder because of their prismatic cleavage. Other minerals, such as serpentine, vary in hardness and in shape of pulverized particles. Most of the major constituent minerals of industrial talc are chemically inert and generally grind to a white powder and have high dielectric constants, therefore, these minerals naturally occuring in varying proportions produce inert light-colored rocks with a range of hardness and particle shape when pulverized, making industrial talc an unusually versatile and widely used mineral product.

USES

Industrial talc is used where certain combinations of the following properties are desired: Extreme whiteness when powdered or fired, softness or smoothness, fibrous or flaky particle shape, various degrees of oil absorption, chemical inertness, high fusion point, low water absorption and shrinkage when fired as a ceramic body, low electrical and thermal conductivity, good retention as fillers, and ease of grinding to extreme fineness (Industrial Minerals, 1968).

Talc in the form of soapstone has been used since prehistoric times for carved cooking utensils; current uses of talc are intimately tied to the demands of a complex industrial society. It is important to the manufacturing and building industries, and periodic fluctuations in consumption are directly related to the economic conditions of those industries.

Talc is used as a ceramic base material for wall and floor tile; as a filler by the plastic, paper, roofing, and rubber, industries; as a paint extender; and as an insecticide diluent and carrier. Other special uses are diverse, ranging from a polish for rice, wood turnings, nails, and white shoes to a dusting powder for salami. In the massive form of soapstone, it is cut for laboratory table tops and sinks, steel-marking crayons, and blocks for art carvings. High-frequency ceramic insulator shapes are machined and fired from another massive variety known as block steatite, and block talc is machined and fired for burner nozzles. Talc and soapstone sold or used in the United States in 1969 and 1970 are listed by use in table 128. Figure 69 shows consumption of talc by the major consuming industries during 1950–70. Talc used for ceramic wall tiles and extender in paint now accounts for half of the annual consumption. The roofing, paper, insecticide, and rubber industries together consume an additional quarter, and the many miscellaneous special uses account for the remainder. The only recent outstanding increase in the consumption of talc is in the "other uses" category in figure 69. This curve since 1966 shows an exponential growth which I attribute to the use of talc as a filler pigment in white plastic insulation, containers, and sheeting.

TABLE 128.—*Talc and soapstone sold or used by producers in the United States, by uses*

[In short tons. From Wells (1970)]

Use	1969	1970
Ceramics	245,704	228,595
Insecticides	53,722	33,697
Paint	166,170	154,265
Paper	54,554	52,328
Roofing	30,526	44,997
Rubber	24,464	28,348
Textile	7,974	6,187
Toilet preparations	12,235	13,721
Other[1]	279,168	289,644
Total	874,517	851,782

[1] Includes asphalt filler, crayons, exports, fertilizer, floor and wall tile, foundry facings, insulated wire and cable, joint cement, plastics, rice polishing, and miscellaneous products.

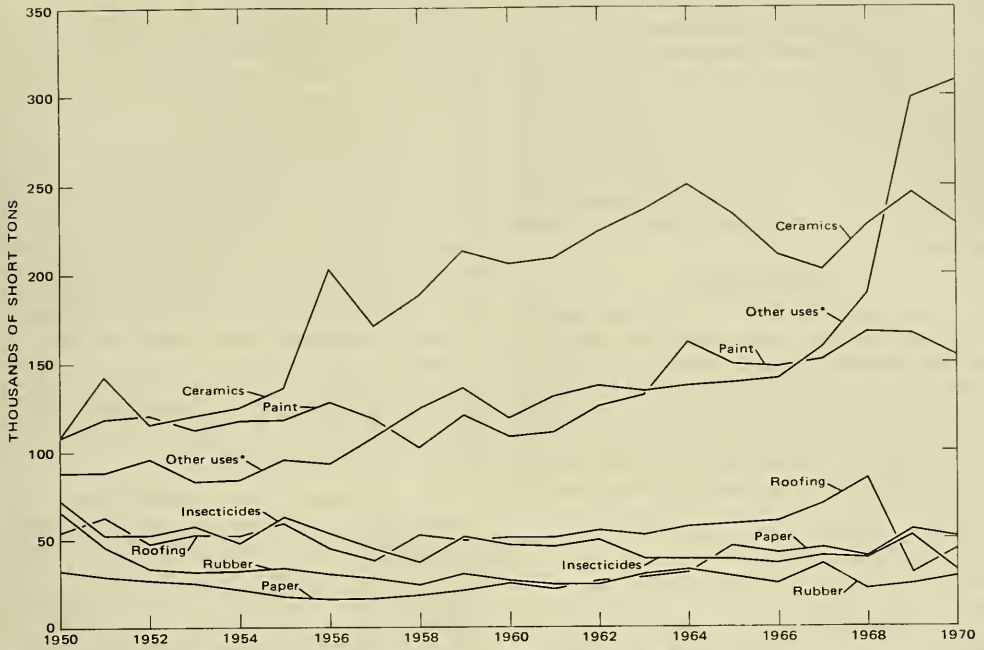

FIGURE 69.—Talc and soapstone produced and used by major consuming industries in the United States, 1950–1970. Other uses include asphalt filler, crayons, exports, fertilizer, floor and wall tile, foundry facings, electrical insulation, joint cement, plastics, rice polishing, textile coating, toilet preparations, and miscellany.

The United States has abundant reserves and resources of talc, but is deficient in certain grades such as block steatite used for high-frequency insulators, and cosmetic talc. In 1970, imports of talc were 29,988 short tons, and exports were about 105,000 tons. Use of flotation and magnetic separation methods in the processing of talc has made us less dependent on imports for cosmetic-grade talc, although in 1970 imports of cosmetic-grade talc from Italy were markedly increased. Phosphate-bonded synthetic "lava" talc and die-formed steatite is being increasingly substituted for block steatite for ceramic insulator needs; however, a residual demand for block steatite for high-frequency insulators will probably continue.

COMPETITIVE MINERALS

Many minerals are competitive with talc for ceramic and filler uses. Kaolin is commonly used as a base for wall tile, but such clay-base tile absorbs water and expands causing the glaze to craze (Gaskins, 1952). Addition of a certain amount of talc to the base material alleviates this condition and improves translucency and toughness of the tile. Another important competitive use of kaolin is as paper filler and coater. Ground limestone is substituted for talc as a paint pigment extender, but it is reactive and does not have the scaly and fibrous particle shape of talc that aids in both coating and holding pigment in suspension. Wollastonite ($CaSiO_3$) has most of the good qualities of talc and is directly competitive in the ceramic and paint industries (Andrews, 1970). However, reserves of wollastonite are relatively small in the United States, and this mineral is now mined only in Essex County, N.Y., and in Riverside and Inyo Counties, Calif. Synthetic molded laboratory work surfaces are increasingly being used as a substitute for sawed soapstone slabs. Some of the synthetic material probably contains talc as a filler, and the overall tonnage of talc consumption may therefore not be seriously decreased, but a much less expensive form of industrial talc will be consumed.

Pyrophyllite, a mineral with physical properties

similar to talc, has many of the same uses as talc and is in fact generally included with talc in resource studies. In the United States it is produced in North Carolina and California (Espenshade, 1962), and in the past 10 years pyrophyllite consumption averaged about 13 percent of talc consumption. Resources of pyrophyllite are much less extensive than those of talc, so although its substitutability for talc is high, its percentage of the industrial talc market probably will not increase significantly.

EXPLOITATION

Talc was used by the Indians and early settlers for cooking utensils carved from soapstone that occurred mainly in altered ultramafic bodies. Mining of talc and soapstone deposits for other uses began in some districts in the early 1800's, but because industrial talc is tied closely to the demands of a modern industrial society, extensive mining has occurred only in about the past 50 years. Figure 70

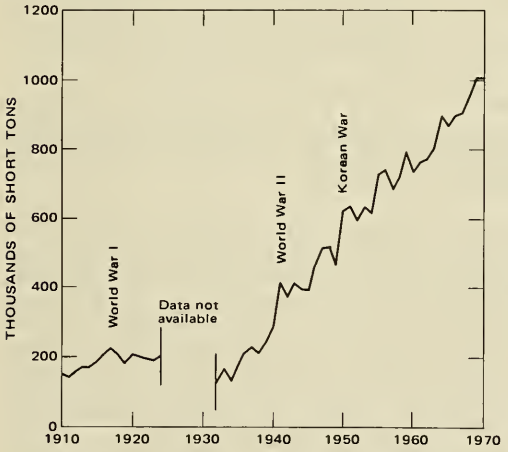

FIGURE 70.—United States consumption of talc, soapstone, and pyrophyllite, 1910–70.

shows the consumption curve for talc, soapstone, and pyrophyllite during 1910–70. The figures are from the Bureau of Mines yearbooks, and the included pyrophyllite ranges from 10 to 15 percent of the total. The graph shows increases during national emergencies and other fluctuations owing to changing economic conditions of industry during more normal periods. The overall slope of the curve is straight and steep.

Because of the diversity of uses for industrial talc, total consumption increases steadily, even when demand for individual consumer products fluctuates drastically. As technology develops new products, such as the widespread use of plastic insulation in place of rubber, the demand for talc as a filler may continue because both plastic and rubber require an inert mineral filler. Likewise, increasing use of talc as a base by the ceramic industry since about 1955 has offset decreased consumption by the rubber and insecticide industries (fig. 69), and the booming use of white plastic by our society has apparently caused an increase in talc consumption as a white filler. Other, more sophisticated uses are being developed; for example talc reduced to minus 50-millimicron particle size was used in a patented method by which an electrically insulating surface layer can be induced by electrophoresis on the exterior of an article that in itself is electrically conducting (Wells, 1970, p. 7).

BYPRODUCTS AND COPRODUCTS

Talc mining generally produces no byproducts. Because of the great variety of talc grades required by different consumers, selective mining, milling, and laboratory control results in high recovery of numerous marketable grades from most deposits. In effect, the many grades of industrial talc are coproducts. Bilbrey (1962, p. 22) reported that a cobalt-nickel concentrate was a byproduct of talc flotation in Vermont for a few years in the 1940's. The U.S. Bureau of Mines "Minerals Yearbooks, 1940–43" indicate a total sale of 109 tons of concentrate containing 1.16 percent cobalt and 12.7 percent nickel. Other potential byproducts are anthophyllite asbestos at Dadeville, Ala. (Neathery and others, 1967), and magnesite from Johnson, Vt. (Cooper and Hartwell, 1970).

The recent discovery of scheelite in soapstone deposits in Madison County, N.C., raises the possibility of coproduction from these deposits. (See "Tungsten.")

ENVIRONMENTAL PROBLEMS

Mining of industrial talc is from both underground and opencut mines. Inasmuch as recovery is higher than that in mining for vein minerals, far less of the landscape is disrupted by the operation, and waste piles are relatively small. Only a few operations, such as at Johnson, Vt., use flotation methods for mineral separation; therefore, most talc mining does not have tailings ponds.

One environmental problem does confront the industry, however; research mainly by a group in

Mt. Sinai School of Medicine in New York City has shown a positive correlation between incidence of lung disease and working with or near asbestos without safety precautions (New York Academy of Sciences, 1965). Because many of the talc deposits mined in the United States contain asbestiform tremolite and anthophyllite, emission-control standards will undoubtedly be established for mining and milling them. The tremolite and anthophyllite content of talc used as a cosmetic or for food processing, such as polishing rice or dusting salami, also will probably be carefully monitored, as will that in talc used as a carrier for pesticide dusts.

GEOLOGIC ENVIRONMENT

Talc and soapstone deposits of commercial importance occur mainly in metamorphosed dolomite and altered ultramafic igneous rocks. These rocks and contained talc deposits are present in metamorphosed terranes throughout the world. In the United States, talc is found in the older Appalachians and Piedmont from New England to Alabama in the east and in California, Nevada, Washington, and Montana in the west (Chidester and Worthington, 1962). Important deposits also occur in Texas, but most of the Central United States, from the Appalachians to the Rocky Mountains, lack a convenient source of industrial talc.

TALC FROM REGIONALLY METAMORPHOSED DOLOMITE

Dolomites with ascociated siliceous sediments can be metamorphosed to form talc. In many deposits derived from sedimentary dolomite and silica, talc forms as a final retrograde hydrothermal phase from earlier magnesian silicates such as tremolite, forsterite, and diopside. These three minerals result from high-grade metamorphism with the addition of silica and limited water. Retrograde alteration of the earlier minerals to talc and serpentine is accomplished hydrothermally with the release of calcite and CO_2.

Most of the major talc deposits in the United States are in metamorphosed dolomite; this type accounts for more than half the total production. The largest producers in the country are mines on such deposits in St. Lawrence County, N.Y., where talc, tremolite, and serpentine rocks occur in Precambrian carbonate and siliceous sedimentary rocks. The talc zones are stratigraphic units that have been tectonically swelled in axial parts of folds and at places are pinched out on fold limbs. Shearing has played a major role in the development of talc schist zones.

Similar talc deposits are in the Murphy Marble belt of North Carolina, the Dillon-Ennis district of southwestern Montana, and the Inyo and Panamint Ranges of California. The deposits in North Carolina are lens shaped and follow a zone of quartzose dolomitic marble. Some of the North Carolina talc is exceptionally white, and locally massive varieties are sawed for steel-marking crayons. The deposits in Montana are rather large but require considerable selective mining and sorting because of interlayered unaltered wallrock. The Montana deposits and those in the Inyo and Panamint Ranges of California provide some rock of steatite or near-steatite grade.

Deposits in the Chatsworth district of Georgia and the Allamoore district of Texas, also formed from metasedimentary rocks, are not so closely related to dolomitic parent rocks. These deposits are associated with phyllites, schists, and quartzites, and required extensive metasomatism for their development.

The Winterboro deposits in Talladega County, Ala., occur in or as residual deposits derived from Cambrian and Ordovician dolomite that is relatively unmetamorphosed. The talc is virtually unfoliated and preserves the crystallinity of the parent rock (Wedow and Sweeney, 1968). These deposits should be studied further because of their low metamorphic grade. Possibly they result from prograde metamorphism, with talc being the highest grade mineral produced, in contrast to other deposits in which retrograde metamorphism was important.

TALC DEPOSITS FORMED FROM ULTRAMAFIC AND MAFIC IGNEOUS ROCKS

Talc deposits associated with serpentinized ultramafic rocks occur in regionally metamorphosed and folded sedimentary and volcanic rocks such as those in the older Appalachian Mountains and Piedmont in a belt from New England to Alabama (Larrabee, 1966, 1971). These deposits generally occur as rinds on serpentine bodies but in places have completely replaced them. Some deposits occur where sodic pegmatites intrude serpentine. Steatitization, the formation of talc-rich-rock, was accomplished by either of two processes—the metasomatic reaction between serpentinite and introduced CO_2 or a metamorphic reaction between serpentinite and siliceous country rock. These two processes, though independent, can work together. Generally, the deposits formed mainly by CO_2 metasomatism have an abundance of talc-carbonate rock; and where metamorphic reaction was important, talc rock is dominant. The largest producing talc mines in altered ultramafic rocks are in Vermont; many similar but

smaller deposits have been mined in the eastern serpentine belts and in California, Texas, and other States.

Talc deposits that formed by intrusion of sodic pegmatites into serpentinite are mined in Harford County, Md. (Pearre and Heyl, 1960, p. 795). Apparently the igneous intrusions provided solution and heat for the reaction with serpentinite to produce a thin contact-zone rind of vermiculite and actinolite, and farther into the country rock, an irregular zone of massive talc rock.

Some talc deposits were formed by pervasive steatitization of mafic rocks associated with ultramafic rocks. At Schuyler, Va., tabular or lenticular bodies of hypersthene gabbro have been altered to greenish-gray soapstone (Hess, 1933). Steatitization here is related either to regional metamorphism or to igneous activity deep in the crust. The altered rock consists of varying proportions of amphibole, chlorite, carbonate, talc, and magnetite and therefore varies from hard to soft. The rock is tough because of an interlocked felted texture of the minerals and is desirable for sawed shapes such as laboratory tables and sinks.

TALC DEPOSITS FORMED BY CONTACT METAMORPHISM OF DOLOMITIC SEDIMENTS

Granite plutons and diabase dikes that intrude favorable dolomitic strata provided the heat and solutions for the steatitization of the sedimentary rocks, and in some places granite itself has been replaced by talc. Southern California contains excellent examples of talc deposits formed by such contact metamorphism. A mining district that extends from the Panamint Range eastward across southern Death Valley to the Kingston Range in Inyo and San Bernardino Counties contains talc deposits that occur mainly along the upper contacts of diabase sills with cherty dolomite of Precambrian age. These ore bodies average 10–25 feet in width and are 1,000 feet to at least 1 mile in length. Most of the talc produced in California comes from them. Wright (1968) presented a detailed description of more than 40 deposits in this district.

Talc deposits of northeastern San Bernardino County in the Silver Lake–Yucca Grove district are genetically associated with granitic plutons. The deposits occur as lenses in a terrane composed of lower Precambrian metasedimentary and intrusive rocks. Dolomitic strata were selectively tremolitized when granitic rocks were emplaced nearby. Subsequently, during retrograde metamorphism, the tremolite was altered to talc schist along the borders of the deposits. The industrial talc in these deposits is snowy white and medium to coarse grained. Minable talc bodies are about 10 feet wide and as much as 800 feet long (Chidester and others, 1964, p. 25).

RESOURCES

IDENTIFIED AND HYPOTHETICAL RESOURCES

The United States is self-sufficient in most grades of talc and soapstone. In the past, we have imported most of our block steatite and cosmetic-grade talc. Because of technical refinements in the use of phosphate-bonded domestic ground talc of steatite grade and die-formed steatite as a substitute for insulator forms machined from block steatite, we are no longer dependent on foreign supplies, and stockpiled material probably will be sold. About half the cosmetic-grade talc consumed (Industrial minerals, 1971) is still imported, but selective-flotation techniques using domestic talc have eliminated much of our dependence on foreign sources.

Chidester, Engel, and Wright (1964) estimated our identified resources at a minimum of 89 million tons, with the possibility of additional discoveries being good to excellent in all mining districts. Resources should be adequate to meet the demands for many decades. The Bureau of Mines, in its Commodity Data Summary of January 1972, estimated United States reserves at 150 million tons and world reserves at 360 million tons. Projected demand for talc in the United States for the year 2,000 by the U.S. Bureau of Mines is 2.28 to 3.36 million tons (Cooper and Hartwell, 1970). Worldwide demand for talc is increasing faster than demand in the United States as societies become more complex, but the world's identified resources appear adequate to meet demand.

SPECULATIVE RESOURCES

Most talc deposits are found in areas of high-grade or contact metamorphism. The deposits in Talledega County, Ala., however, are in relatively unmetamorphosed Cambrian and Ordovician dolomite. Similar dolomites exist at many other places in the United States. The Alabama deposits should be carefully studied to determine their genesis so that similar deposits might be predicted elsewhere. Many areas of dolomitic marble in the southeastern Piedmont, such as the Wakefield and Cockeysville Marbles in Maryland, might contain talc deposits. Another intriguing possibility is the dolomite and marble units in areas of Precambrian rocks in Wisconsin and Michigan. For example, the Randville Dolomite in Dickinson County, Mich., locally consists of white tremolitic marble (James and others,

1961, p. 128), although this formation at most places is not metamorphosed. This area is particularly important as a potential source of industrial talc because of its proximity to the industrial areas of the Middle West, which are hundreds of miles from all current sources of talc.

PROSPECTING TECHNIQUES

Detailed geologic mapping is currently the best technique in prospecting for industrial talc. For deposits derived from dolomite, the stratigraphy and structure must be known in order to predict the occurrence of talc zones in the subsurface; for instance, previously unknown deposits were recently identified in the town of DeKalb in St. Lawrence County, N.Y., through use of 1:12,000-scale geologic mapping (Brown, 1969; Bannerman, 1972). Although these deposits are exposed at the surface, estimation of continuation to depth can only be attempted through an understanding of the geologic structure. Where talc is a product of contact metamorphism, such as along the diabase sills in the southern Death Valley region, detailed knowledge of the location of dolomitic sediments and diabase sills is important for the location of talcose zones and prediction of their continuation in the subsurface. For deposits formed from ultramafic rocks, too, detailed geologic mapping is important. Geophysical methods, mainly magnetic, can be applied to help locate the parent ultramafic rock. Detailed geologic mapping and drilling then are needed to find talcose zones.

For most of the ceramic and filler grades of talc, the consumer industries have rigid chemical and physical specifications for the milled rock. Therefore, after a deposit is located, considerable careful testing of chemical and physical properties is required to ascertain the minable parts of a deposit.

PROBLEMS FOR RESEARCH

Even though the resources of talc in the United States are large, restrictive specifications of color and other properties make many deposits unusable for high-priced grades of talc. Sampling and laboratory testing of all known talc deposits would establish the quality and marketability of known resources. As already discussed, new deposits are likely to be found primarily as a result of detailed mapping in geologically favorable terranes. A program of concurrent field and laboratory research is at present being conducted by the North Carolina Department of Conservation and Development for deposits in Madison County, N.C. (L. S. Wiener, written commun., 1972), and a similar study recently was completed for Tallapoosa and Chamber Counties, Ala. (Neathery, 1968).

Industrial talc is an extremely versatile mineral product, and new uses are continually being found. Close cooperation between the research laboratories of the manfacturers and those of the mining companies could probably develop even more functional grades of talc depending on the demands of new products. Research on new pulverizing techniques capable of producing submicron particle sizes would help in opening new markets, as consumers seem to desire ever finer material despite the high costs.

High reflectance or whiteness is a required quality of industrial talc used in the ceramic, paint, paper, and a few other industries. During the quest for this higher priced product, much subgrade rock is discarded. Some of the waste could be sold locally for mineral filler not requiring white rock, such as in rubber, roofing, insecticide, and some dusting applications. Some progress has apparently been made in improving the color of off-white talc (Wells, 1970). More research in this field is needed.

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TELLURIUM

By D. F. Davidson and H. W. Lakin

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ABSTRACT OF CONCLUSIONS

The present demand for tellurium is less than the amount available as a byproduct from the copper and lead industries. A shortage of tellurium could develop as a result of a change in the processes of recovery of copper from its ores. In-place leaching of copper from its ores leaves the associated tellurium undissolved in the waste rock resulting from the process. Thus, as the use of the leaching process increases at the expense of smelting, the supply of tellurium will decrease.

Identified resources of copper in the United States are estimated to contain about 13.5 million pounds of recoverable tellurium. Tellurium may be recovered as a byproduct in burning of coal in huge powerplants, paying in part for environmental improvement. The major resource of tellurium is found in manganese oxide nodules on the ocean floors.

INTRODUCTION

Tellurium was discovered in a complex group of gold telluride minerals in the ores of Transylvania by F. J. Müller von Reichenstein in 1782. It is characteristic of tellurium to form its own minerals in metallic sulfide deposits, although it is very rare.

Tellurium is a nonmetallic element; its atomic number is 52 and atomic weight 127.6; and it exists in eight stable isotopes. It has a specific gravity of 6.24 and melts at 452°C. Tellurium can be obtained in an amorphous or a crystalline form. Amorphous tellurium is brown to black and is produced by reduction of tellurium solutions. Crystalline tellurium has a trigonal structure, is grayish white, lustrous, and brittle, and is produced by casting the molten element. In a thin film, tellurium is dull purple; its vapor is orange yellow.

USES

Tellurium is marketed as a steel-gray powder, and in slabs, tablets, and sticks. The usual commercial grade is about 99.7 percent tellurium with selenium and copper as the principal impurities. Grades of 99.99+ and 99.999+ percent tellurium are available. About 18 percent of the tellurium produced is sold as copper tellurium alloys (40–50 percent tellurium) and ferrotellurium (50–58 percent tellurium) (Lausche, 1967).

About 80 percent of the 221,000 pounds of tellurium used in the United States in 1968 went into the primary metal industries. Low-carbon steels containing 0.02–0.2 percent tellurium have better machinability. Tellurium is also used in iron or steel to reduce the adsorption of nitrogen, to act as a weak deoxidizer, and to minimize pinhole porosity. Less than 1 percent tellurium in copper improves machining properties of the copper without effecting the electrical conductivity or hot working properties of the metal. Lead containing 0.05 percent of tellurium has added resistance to corrosion.

The rubber industry accounted for about 10 percent of the tellurium used in the United States in 1968. Tellurium is used both as the element and as tellurium diethyldithiocarbamate in synthetic and

natural rubbers to increase the resistance to heat and abrasion, to decrease vulcanization time, and to improve the aging properties of the elastomer.

The remaining 10 percent of the tellurium consumed in 1968 goes into many diverse but important uses. Tellurium is used as a catalyst in oxidation, hydrogenation, dehydrogenation, chlorination, dechlorination, hydroxylation, and phenol condensation. Noteworthy properties of tellurium catalysts are selectivity, good yield, and resistance to poisoning. Tellurium has been used as a colorant in ultramarine, black, blue, red, and brown glasses and ceramics. Organic tellurides have been used as antioxidants for lubricants, greases, hydraulic fluids, and hydrocarbon fuels. Tellurium compounds are used as antimicrobial and therapeutic agents. Cyclotelluropentane-3, 5-diones, and various derivatives are very powerful germicides. Tellurium has been used in the treatment of leprosy with good results. Tellurium dioxide suspensions are effective in the treatment of seborrheic dermatitis of the scalp. Tellurium is also used in blasting caps, batteries, thermoelectric devices, solar cells, infrared windows, and semiconductor devices.

Selenium may be used as a substitute for tellurium in metallurgy, ceramics, rubber, and thermoelectric devices. Lead may be used to achieve machinability in steel and thus replace tellurium.

CRUSTAL ABUNDANCE

The crustal abundance of tellurium is unknown. The element is so rare that analytical methods have not been devised with sufficient sensitivity to determine tellurium in igneous rocks with adequate reliability. Efforts have been made to estimate the abundance of tellurium on the basis of selenium-tellurium ratios in materials containing enough of both elements to be measured, but this gives rise to a second-generation error because the abundance of selenium is arrived at similarly by use of sulfur-selenium ratios. Recent estimates of the abundance of tellurium are 0.001, 0.002, and 0.00X ppm (parts per million). The selenium-tellurium ratio in copper produced from porphyry copper deposits in the United States is 1 to 0.4, or 2.5 to 1; the same ratio for Sudbury ores of Canada is 15. Using 0.05 ppm as the crustal abundance of selenium, the ratio of 2.5 gives 0.02 ppm tellurium for the U.S. porphyry copper ores and 0.003 ppm tellurium for the pyrrhotite-chalcopyrite-pentlandite ores of Sudbury. This divergence in the selenium-tellurium ratios is indicative of fundamental differences in the geochemistry of these elements.

GEOCHEMISTRY

Sulfur, selenium, and tellurium belong to the same family of elements; their physical and chemical properties change progressively from the low atomic weight sulfur through selenium to tellurium. An example of how progressive change in physical properties can affect dispersion of these elements in volcanism is found in the boiling points of pertinent chemical forms. The boiling points of sulfur, selenium and tellurium are 444°, 688°, and 1,390°C respectively. Hydrogen sulfide is a stable gas at ambient temperature; hydrogen selenide decomposes in moist air to give selenium and water; hydrogen telluride is even less stable than hydrogen selenide. Whereas sulfur dioxide is a relatively stable gas at ambient temperatures, both selenium and tellurium dioxides are solids that sublime at 317° and 450°C respectively. It is evident from these differences in the three elements that sulfur is very mobile and may be carried in the atmosphere great distances. In contrast, tellurium will be found close to the volcanic source.

Differences in ionic radii materially alter the distribution of tellurium from the distribution of sulfur and selenium. The ionic radius of S^{-2} is 1.84 A, of Se^{-2} 1.98 A, and of Te^{-2} 2.21 A. Selenium can readily substitute for sulfur in sulfide minerals but the tellurium ion is too large to replace sulfur. Consequently selenium occurs in sulfide minerals and selenide minerals in isomorphous association with sulfide minerals, whereas tellurium forms its own minerals as tellurides.

The minimum radius ratio

$$\left(\frac{\text{radius of cation}}{\text{radius of anion}}=0.414\right)$$

for stability of coordinated octahedrons with a ligancy number of 6 (Pauling, 1960, p. 544–545) permits the metals gold, silver, bismuth, mercury, platinum, palladium, and lead to form stable crystalline tellurides, whereas tellurides of zinc, copper, nickel, and iron are less stable. The metals gold-lead listed above, with very large ionic radii, cannot readily substitute in sulfides of zinc, copper, nickel, and iron, nor can tellurium substitute for sulfur; consequently, the rare metals gold, silver, bismuth, mercury, platinum, and palladium tend to accumulate in residual ore fluids and to crystallize as tellurides after most of the sulfide minerals have crystallized. This sequence appears to occur in early magmatic sulfide deposits of the Sudbury (Canada) and Merensky Reef (Africa) types in which platinum, palladium, and bismuth tellurides are conspicuous, as well as in the late-stage, low-temperature hydro-

thermal deposits of the telluride ores of Boulder County, Colo., in which gold and silver tellurides are abundant (Kingston, 1966; Kelly and Goddard, 1969).

Sindeeva (1964) observed that tellurium forms its own minerals in many diverse types of ore deposits. In lead-zinc deposits she reported that tellurium concentrates in galena in microscopic segregations of altaite (PbTe) and hessite (AgTe). The tellurium in copper deposits is associated with chalcopyrite and may occur as microscopic segregations of hessite inasmuch as there is more silver in such ore than required to accommodate all of the tellurium usually found in the ore (Cooper, 1971, table 2–1, p. 15).

In the zone of active oxidation at or near the surface, tellurium is readily oxidized to tellurites (TeO_3^{-2}) from tellurides (Te^{-2}) throughout the normal pH range (3–8). At relatively high, but feasible, oxidation potentials, tellurites are oxidized to tellurates (TeO_4^{-2}) in alkaline environments (pH 6–8.5). This oxidation is verified by minerals consisting of ferric tellurite $Fe_2(TeO_3)_3$ and lead, bismuth, ferrous, and mercurous tellurates. The ready oxidation of tellurides gives rise to the dispersal of tellurium in ground water, from predominantly telluride deposits.

In acid environments produced by the oxidation of pyrite, tellurium is captured in the iron oxide gossans, presumably as basic ferric tellurites. Gossans have been found that contain as much as 1 percent tellurium.

Tellurium is not known to be essential for animal or plant life. It occurs in minute quantities in plants and animals but below concentrations that are readily measured. To illustrate, a limber pine (*Pinus flexilus*) was found to contain 0.05 ppm tellurium in twigs, 0.012 ppm in bark, and $\leq$ 0.005 ppm in the wood (Hubert, 1971). This tree was collected in the Cripple Creek mining district, Colorado, where the ore consisted of gold tellurides and where soils are unusually rich in tellurium; the soil in which it grew contained 0.5 ppm tellurium to a depth of 24 inches and 1 ppm tellurium in the 24- to 30-inch layer.

No tellurium has been found in phosphate deposits, Colorado Plateau uranium deposits, sedimentary sulfur, or sedimentary sulfides. Tellurium is found in the fly ash (as much as 0.2 ppm) of the powerplants burning coal. The selenium-tellurium ratio in coal used in certain southwestern U.S. powerplants ranges from 50 to 100. This ratio indicates a depletion of tellurium with respect to selenium.

Although inadequate analytical methods hamper studies of these materials it is easily established that the selenium-tellurium ratio is much larger in organic-rich sedimentary materials than in their assumed crustal abundance. One must conclude that in the weathering processes, tellurium is dispersed and is not reconcentrated again as selenium is in biosinks.

RESOURCES

Tellurium is obtained primarily as a byproduct of copper refining; 80 percent of the production in the United States is derived from the anode mud deposited during electrolytic refining of copper. Blister copper contains an average of 0.02 percent tellurium or 0.4 of a pound of tellurium per ton of copper, but actual recovery of tellurium is about 0.17 of a pound per ton of copper. Thus, the production of tellurium in the United States, and in most of the world, is directly related to the production of copper. In-place leaching processes for the recovery of copper do not result in tellurium recovery, and the increasing use of these processes could reduce the supply of tellurium materially. Other countries with major potential resources of tellurium are those with major potential resources of copper: Chile, U.S.S.R., Zambia, Peru, Zaïre, Canada, and Mexico (Ageton, 1970; see also "Copper" chapter). Substantial amounts of tellurium are recovered from lead ores.

Resources of tellurium estimated to be potentially available in the identified resources of copper, lead, and coal in the United States and in other countries together with the tellurium available in oceanic manganiferous nodules are shown in table 129.

In electrolytic refining of blister copper about 42 percent of the contained tellurium is recovered from the slime residue. Using the ratio of 0.17 of a pound of tellurium per ton of copper produced, we estimate a total of 13.5 million pounds of tellurium available in identified copper resources of the United States, and 43.9 million pounds available in identified copper resources of the rest of the world.

Refining of lead ores accounts for about 20 percent of the present production of tellurium or one-

TABLE 129.—*Tellurium resources (in thousands of pounds) potentially available in identified resources*[1] *of copper ores, lead ores, coal, and oceanic manganiferous nodules*

Source[2]	United States	Other countries
Copper ores[3]	13,500	43,900
Lead ores	3,000	10,000
Coal	47,400	237,600
Oceanic manganiferous nodules	1,980,000	

[1] Identified resources: Specific, identified mineral deposits that may or may not be evaluated as to extent and grade, and whose contained minerals may or may not be profitably recoverable with existing technology and economic conditions.
[2] Identified resources from respective chapters of this volume.
[3] Assuming 42-percent recovery of tellurium.

fourth of the tellurium from copper resources. The values for tellurium from lead ores given in table 129 are about one-fourth of the resources from copper ores. On the basis of 140 million tons of lead, this estimate requires 1.3 pounds of tellurium per ton of lead; the estimate is probably high.

The average content of tellurium in coal is taken at one-hundredth of the selenium estimate or 0.015 ppm (parts per million) tellurium; this value is probably low, but is significant as a reserve because tellurium would be recoverable with selenium. In table 130 the average tellurium content of coal used in four operating powerplants in Western United States is given, together with the tonnages used per year. The calculated tellurium content ranges from 0.002 to 0.025 ppm, and we find 613.8 pounds of tellurium in 20.35 million tons of coal; in the same coal we found 66,300 pounds of selenium which gives a ratio of about 100 selenium to 1 tellurium. Using this ratio the estimated annual release of tellurium from the combustion of coal in the United States is about 80,000 pounds. All, or virtually all, of this tellurium would be contained in the fly ash.

TABLE 130.—*Tellurium content (in pounds) of annual coal consumption (in millions of tons) at four operating powerplants in Western United States*

[Data from U.S. Geol. Survey, 1972]

Location of powerplants	Annual consumption coal (in millions tons)	Calculated Te [1] content coal (in ppm)	Total tellurium content of annual coal consumption (in pounds)
Four Corners, N. Mex	7.0	0.025	350.0
Cholla, Ariz	.4	.002	1.6
Mohave, Nev	6.7	.013	187.2
Hayden, Colo	6.25	.006	75.0

[1] Calculated from tellurium in fly ash and fly ash = 0.75 total ash.

Tellurium is enriched in oceanic manganese oxide nodules. The median tellurium content of 12 samples from diverse locations in the Pacific and Indian Oceans is 30 ppm (Lakin and others, 1963). If it is assumed that manganese oxide nodules contain only 10 ppm tellurium and we have an estimated 90 billion tons of nodules, then there is a potential resource of 1,980 million pounds of tellurium in these ocean deposits.

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THALLIUM

By Keith Robinson

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ABSTRACT OF CONCLUSIONS

Thallium, a soft, heavy, readily oxidizable metal, is recovered as a byproduct from the flue dust and residue produced in the smelting of base metals, principally zinc. A 75-percent recovery factor has been calculated.

The current uses for thallium are limited, being primarily confined to electronics and metallurgical processing; lesser applications are in glass, explosives, agriculture, and medicine.

U.S. and total world identified resources of thallium from zinc, lead, and iron sulfides are estimated at 266 and 1,390 tons respectively. Additional U.S. and total world resources contained in coal ash are 119,000 and 715,000 tons. Identified manganese nodules occurring on the sea floors are estimated to contain 9.9 million tons of thallium. Assuming no unforeseen demand, the world supply of thallium from identified zinc sulfide sources will be exhausted in 43 years at the present rate of consumption, and from all identified sulfide sources in 70 years.

Evidence suggests that the variable abundance of thallium in specific minerals may, in part, be controlled by temperature and pressure. This could prove valuable in delineating the mineralized potential of areas for other commodities.

INTRODUCTION

Thallium was recognized and named as a new element by Sir William Crooks in 1861 while making a spectroscopic search for tellurium in seleniferous deposits from a sulfuric acid plant in the Hartz Mountains of Germany. He named the newly discovered element "thallium," from the Latin word thallus, meaning budding twig, because its bright-green spectral line was the color of young vegetation.

Thallium metal is extracted and refined as a byproduct from the flue dust and residue produced in the smelting of base-metal ores. Zinc ore is the primary source of thallium metal. It is estimated that approximately 75 percent of the thallium is recovered from the processed flue dust and residue. In addition, thallium is recovered from the smelting of other base metals such as lead, and may also be recovered from the trace amounts occurring in pyrite, during the roasting of pyrite to produce sulfuric acid.

The most important, nontoxic, uses of thallium are in the electronic and metallurgical processing industries; lesser uses are in glass, explosives, agriculture, and medicine.

Pure thallium has poor mechanical properties, but when introduced into other metals in small quantities it can significantly improve their mechanical and electrical properties. Thallium improves the hardness of lead, and its alloy with lead is corrosion resistant; its alloy with copper is heat resistant and of high electrical and thermal conductivity; and its alloy with aluminum and zinc improves the abrasion resistance of bearings, particularly in the absence of petroleum lubricants—a property which may have considerable application in the aerospace program. The presence of thallium as micro-occlusions improves the machinability of stainless steel. It is used with indium, mercury, and gold in solders for ceramics and semiconductors. The quality of furnace

linings in aluminum smelters is improved by the addition of thallium. Thallium is also used to modify the pore size of molecular sieves by partial cation exchange. Thallium has extensive electronic applications, being used in the construction of photoelectric cells and exposure meters to detect infrared radiation, particularly in military communication systems. It is used as an integral part of scintillation spectrometers, in thallium-activated sodium iodide crystals, where it reduces background noise in the detection of gamma radiation and in measuring high-energy electrons for X-rays. The performance of rectifiers is also improved by utilization of a selenium-thallium alloy in the cathodes. Thallium is used in electrical resistors and superconductors, in tungsten filaments and radiation sources in X-ray fluorescence, and in the production of illuminated phosphors. The inclusion of thallium in mercury vapor lamps has increased their service life and almost doubled their illumination output. It has also been tested in lamps producing radiation in the suntan range. The refractive index of optical glass is increased by the inclusion of thallium. It is also used with other metals and as an oxide to glaze semiconductors, capacitors, printed circuits, and other electronic devices to protect them from atmospheric deterioration and contamination. As a catalyst in electroplating, thallium improves the adherence and uniformity of gold coatings on semiconductor devices. Technological advances have been made in the use of thallium in alloys for low-temperature thermometry. Thallium has also been utilized in explosives as TlN_3, in medicine to treat ringworm, and in agriculture. In experiments conducted in Russia, Kolotova and Kharitonova (1970) found germination and leaf growth were promoted in seeds soaked with 0.001 percent Tl_2SO_4 solution, resulting in a 13-percent increase in corn yield and a 43-percent increase in carrot yield. A solution of 0.05 percent is toxic.

Current application and use for thallium are wide but limited; U.S. domestic production can exceed demand, and immediate reserves are substantial. Thus, thallium is not a high-priority material and no government-sponsored stockpiles exist. To some extent, current use and demand for thallium are limited by the need for additional comprehensive research into its complete chemical and physical properties and into its utilization potential. Lee (1971) expects its future industrial use to be one of a reaction intermediate in various syntheses, utilizing to advantage the oxidizing power of Tl^{+3} and the stability of many Tl^{+1} derivatives. The highly toxic nature of thallium salts is a deterrent to its use, and adequate substitutes are available for some of its present applications, particularly in rodenticides and insecticides and in electronics. Hence, the national and world economic importance of thallium is relatively low. Possibly, however, new technological advances in the use of thallium and its compounds will change this situation. Furthermore, the variable abundance of thallium in specific minerals may prove a valuable index to the economic potential of mineralized areas for other commodities.

World production of zinc ores containing thallium is adequate for the current demand. It is doubtful, however, that any substantial future or sudden need for thallium could be met by increased processing of residues and flue dusts from the smelters and (or) by improving the recovery factor. This fact implies that alternative sources of thallium must be established soon.

Present estimates of the world consumption of thallium are as much as 15 short tons annually, of which the U.S. requirements are given as 3.25 tons. The United States now refines enough thallium to meet domestic demand, although an estimated 50 percent is obtained from zinc ores imported from Canada. U.S. imports of zinc ores containing thallium are mostly from Canada; lesser amounts are from Mexico, Peru, Australia, and other countries. The current shutdown of domestic smelters, however in conjunction with expanded smelting capacity in Canada, Mexico, Australia, and Japan, may soon change the sufficiency of domestically refined thallium metal to complete dependence on imported sources.

EXPLOITATION

The first recorded use of thallium salts was in medicine in 1896. In 1919 thallium salts were used in the manufacture of photosensitive cells. In 1920 they were used as a rat poison in Germany, and in 1925 the principal worldwide use of thallium salts became that of a rodent poison and insecticide in the form of thallium sulfate, an extremely toxic, odorless, and tasteless chemical. This practice was curtailed in the United States by a 1965 Federal ruling, because of the extreme toxicity of thallium salts to humans. Lee (1971) stated that thallium sulfate is a cumulative poison which may be absorbed by the skin. A human lethal dose is about 1.75 grams, death occurring in a few days through respiratory failure after convulsions and delirium.

The sparsity of characteristic thallium minerals and its highly dispersed nature have prevented thallium from being found in concentrations of sufficient magnitude to be mined as the principal ore

material. As a group, potassium-rich silicates contain the greatest and most consistent amounts of thallium, but these minerals have little or no commercial value in the metallurgical processing industry at this time. Thus, as Greenspoon (1970) stated, the exploitation of thallium is an integral function of zinc production and demand. To date, world consumption of thallium has been less than the amount that could be produced as a byproduct from base-metal sulfides.

Except for two periods of marked increase in demand, one in the late-middle 1950's and one in the early-middle 1960's, U.S. consumption of thallium has been relatively stable, approximating 4,000 pounds annually. Greenspoon (1970), however, indicated that the 1968 demand for thallium had risen to 6,500 pounds. She gave values of annual peak demand for thallium in the mid-1950's at approximately 14,000 pounds and in the mid-1960's at some 9,000 pounds. The 1950's demand probably resulted from increased research using radiation equipment and from sophistication of military defense systems, particularly infrared detection. The increased demand in the mid-1960's may have been due to the conversion of domestic electronic equipment to solid state and increased use of thallium in or associated with electronic components. The sudden drop following this increase in demand was probably due to the Federal curtailment on the use of thallium as a rodenticide. From 1964 to 1968 no thallium was produced in the United States, presumably because processed reserves were sufficient to meet requirements. Thus, production is sporadic. It is likely that industrial plants that use thallium buy sufficient amounts at any one time to last several years. As a consequence, production/time curves are erratic and of no meaningful significance.

GEOLOGIC ENVIRONMENT

GEOCHEMISTRY

Thallium, atomic number 81, atomic weight 204.39, occurs next to lead in the periodic table and the two metals exhibit similar physical properties. There are two naturally occurring stable isotopes of thallium, Tl^{203} and Tl^{205}, their relative abundances being given as 29.46 and 70.54 percent respectively. Thallium metal is bluish white to silvery white and, like lead, is soft and malleable. Unlike lead, however, a fresh-cut surface of thallium metal will develop a thick oxide coating in several weeks. The density of thallium is 11.85 g/cm^3 at 20°C, the melting point is 303°C, and the boiling point is 1,457°C. Thallium metal occurs with three crystal lattice modifications: below 230°C it is hexagonal close-packed, above 230°C it is body-centered cubic, and at high pressures it is face-centered cubic, the triple point being at 110°C and 30 kilobars.

Shannon and Prewitt (1969) gave the following ionic radii for thallium in various coordination polyhedra.

	Coordination No.	Ionic radius (A)
Tl^{+1}	VI	1.50
	VIII	1.60
	XII	1.76
Tl^{+3}	VI	.88
	VIII	1.00

Thallium was placed in group III of the periodic table by Mendeleev, under boron, aluminum, gallium, and indium. Thallium has three electrons in its outer valence shell and the maximum positive valence state attained is Tl^{+3}, by donation of the two outer $6s^2$ and single $6p^1$ electrons to coordinating anions. The thallic state is generally attained under highly oxidizing conditions. The single $6p^1$ electron, however, is much more readily donated than the two $6s^2$ electrons, so that under more normal endogene processes, thallium is preferably in the monovalent Tl^{+1} or thallous state. Thallous (Tl^{+1}) salts are generally highly volatile.

In the monovalent state, thallium has unique chemical and physical properties, resembling both lead and the alkali metals potassium, rubidium, and cesium. Thus, thallium is both a chalcophile and a lithophile element, and under certain conditions displays considerable siderophilic affinities. As a consequence it is widely dispersed in the earth's crust. Vlasov (1964, p. 491–680 of English translation) stated that thallium metal closely resembles lead in density, melting point, electrical conductivity, hardness, atomic volume, radius, and thermal stability. Like lead and other chalcophile elements, thallium is also diamagnetic. Similarly, monovalent thallium resembles the alkali metals potassium, rubidium, and cesium of the lithophile group in both physical and chemical properties. It replaces K^{+1} by isomorphous substitution in silicates such as the alkali feldspars and micas, and in some minerals such as pollucite it is thought to replace Rb^{+1} and Cs^{+1} (Ahrens, 1947a). Several authors have attempted, with limited success, to establish Rb/Tl and K/Tl ratios on basic through acidic and pegmatitic igneous rocks. In some instances there is a suggestion of a direct linear relationship between rubidium and thallium (Ahrens, 1948) and the suggestion of an inverse linear relationship between potassium and thallium.

The crustal abundance of thallium is low, approximating 1 ppm (part per million). Estimates of the average crustal abundance of thallium range from 3 ppm (Ahrens, 1947b) to values as low as 0.1 ppm (Noddack and Noddack, 1934). An average value for all estimates approximates 1 ppm, which is in agreement with the values of 1.3 ppm given by Shaw (1952, 1957) and of 1–1.1 ppm by Ivanov (in Vlasov, 1964). Although the abundance of thallium is extremely low, it is in excess of the crustal abundances of elements such as mercury, silver, and gold. Unlike these elements, however, thallium rarely concentrates into specific minerals. Several characteristic thallium sulfide, selenide, and oxide minerals occur in nature, but they are extremely rare; most thallium occurs as a trace element in other minerals.

The occurrence and concentration of thallium appear to be functions of genetic environment and elemental association. These conditions, in turn, are governed by chemical affinity, atomic size, valency, and temperature and pressure.

DISTRIBUTION IN MINERALS AND ROCKS

The main source of thallium metal is sulfide ore, mined primarily for base metals such as lead and zinc that yield thallium as a byproduct. The thallium content of these sulfides ranges from 10,000 ppm to nondetectable amounts. The most consistent occurrence of thallium is in the structure of the alkali feldspars and some micas, in which values range from 600 ppm to nondetectable amounts; these silicate minerals have little or no present economic significance.

Vlasov (1964) noted that although thallium occurs in sphalerite, pyrite, marcasite, chalcopyrite, pyrrhotite, and other sulfide minerals, it is particularly concentrated in the colloform varieties. Thus it may be possible to explain the wide variation of thallium content in specific sulfide minerals in terms of temperature and pressure—those sulfides formed from a crystallizing melt generally being low in thallium, and those formed from colloidal suspensions under lower temperatures and pressures generally being enriched in thallium, with intermediate variations between these end members.

Because of chemical affinity, size, and valency, thallium associates with silicate minerals rich in the alkali metals potassium, rubidium, and cesium. The isomorphous substitution of thallium for potassium is readily attained in the alkali feldspars and in the micas where potassium is contained as the relatively loosely bound, high coordinated interlayer cation. Hence their thallium content may be quite high, in the hundreds of parts per million, especially in the later-stage pegmatitic alkali feldspars and micas.

In minerals of sedimentary origin, many manganese hydroxides contain concentrations of thallium with values as high as 2,300 ppm. Substantial thallium content has also been recorded in pyrites of sedimentary origin, particularly those associated with coal beds.

Thallium is widely dispersed in rocks, but its distribution is controlled by its general restriction to the sulfide and alkali-rich silicate rock-forming minerals. Thus its concentration in ultrabasic rocks is very low, less than 1 ppm, increasing gradually through intermediate to acidic and pegmatitic rocks to concentrations greater than 1 ppm. Thallium appears to increase in direct relationship to an increase in alkali feldspars and potassium-rich micas. In particular, it is noted to concentrate in the later stage, lower temperature pegmatites and aplites.

The relationship of thallium to metamorphic rocks is poorly understood. On the basis of characteristic mineral assemblages, particularly those rich in the alkali metals, it would appear logical for thallium to decrease with increasing metamorphic grade in an open system.

In the sedimentary cycle, the behavior of thallium is complex. Thallium may occur in a detrital grain of the original host mineral, such as a feldspar or mica. It may also occur as a constituent of those minerals formed in the sedimentary environment—in highly oxidizing conditions incorporated into manganese hydroxides, in reducing conditions as a sulfide in colloidal pyrite, and in a marine environment preferentially absorbed by colloidal clays and shales.

Thus thallium values range from 6 ppm, recorded in a shale, to nondetectable values in carbonate rocks.

RESOURCES

World reserves and potential resources of thallium (table 131) were calculated from respective commodity reserve and resource estimates prepared for this volume (except for iron sulfides, which were based on U.S. Bureau of Mines estimates), using thallium contents of 2.2 ppm in zinc sulfides, 2 ppm in lead sulfides, 0.25 ppm in iron sulfides, 0.75 ppm in coal ash, and 10 ppm in manganese nodules—factors computed from recently processed analytical data of a study of the distribution and occurrence of thallium in rocks and minerals.

The United States is potentially self-sufficient in thallium resources, the reserves contained in zinc, lead, and iron sulfides being 266 short tons, and

TABLE 131.—*World reserves and potential resources of thallium, in short tons*

Reserves: Identified deposits from which minerals can be extracted profitably with existing technology and under present economic conditions.
Potential resources: Identified mineral deposits not profitably recoverable with existing technology and economic conditions, and undiscovered mineral deposits whether of recoverable or subeconomic grade.
Identified resources: Specific, identified mineral deposits that may or may not be evaluated as to extent and grade, and whose contained minerals may or may not be profitably recoverable with existing technology and economic conditions.
Hypothetical resources: Undiscovered mineral deposits, whether of recoverable or subeconomic grade, that are geologically predictable as existing in known districts.

Reserves

Source	Zinc sulfide	Lead sulfide	Iron sulfide	All sulfide
U.S.A.	165	88	13	266
Other North American	143	48	15	206
South America	59	14	26	99
Europe	198	58	50	306
Russia	106	42	40	188
Asia	70	24	36	130
Australasia	77	44	1	122
Africa	51	12	10	73
World total	869	330	191	1,390

Potential resources

In zinc sulfide, worldwide		17,818
In lead sulfide, worldwide		3,944
In oceanic manganese nodules		9,900,000
In coal ash from identified coal resources:		
U.S.A.	119,000	
Other North American	11,000	
South America	1,500	
Europe	47,000	
Russia	488,000	
Asia	38,000	
Australasia	4,500	
Africa	6,000	
Total coal ash, identified resources		715,000
In coal ash from hypothetical coal resources		550,000

resources contained in coal ash being 119,000 tons. The coal ash, however, is a highly dispersed source and probably most thallium will continue to be obtained as a byproduct from zinc ores. No published data could be found on the recovery factors attained in the processing of thallium from the flue dust and residues of base-metal smelting. Previous authors have inferred the recovery factors to be low. Converting the total 1968 U.S. smelter production of zinc to sulfide, calculating the hypothetical thallium amount this sulfide should contain, and then comparing this value with the estimated amount of thallium actually extracted in 1968, produces a recovery factor of approximately 75 percent. This is considered a realistic value and a minimum if the assumed average thallium content of zinc sulfide at 2.2 ppm is correct. It is certainly not low, as previously stated.

U.S. recoverable thallium reserves from zinc sulfides, employing present technology, are estimated at 124 tons, and from all sulfides, 200 tons. At a domestic consumption rate of 3.25 tons annually, the supply is sufficient for 38 and 62 years respectively. The present supply of thallium-bearing zinc ores slightly exceeds the requirements for thallium metal, and unprocessed residues containing thallium are being stockpiled by the industry. Any unforeseen increase in the demand for thallium, however, would command that alternative sources other than zinc sulfides be considered. In this respect the vast potential of coal ash and sea floor manganese nodules is important.

The United States refines approximately 20 percent of the world's output of thallium metal to meet domestic requirements. This percentage must surely decrease with continuation of the current trend toward closing of domestic smelters and expansion of zinc-smelting facilities in Canada, Mexico, Australia, and Japan, together with the capability of extracting thallium as a byproduct.

Total world reserves of thallium contained in zinc sulfide reserves are estimated at 869 tons, of which 650 tons is recoverable with a 75 percent recovery factor. At an estimated world consumption rate of 15 tons annually, the supply is sufficient for 43 years. Projected world reserves of thallium from all sulfide sources, 1,390 tons, will be exhausted in 70 years under the same conditions. Total world thallium resources contained in coal ash from identified coal resources are estimated at 715,000 tons, and in sea-floor manganese nodules a massive 9.9 million tons. Increased discovery of sulfide deposits will proportionately increase thallium reserves, and potential resources are very high, particularly in relatively unexplored areas. In addition, the inclusion as speculative resources of the thallium contained in pegmatitic feldspars and micas, which could be recovered should the need arise, produces vast potential resources.

PROBLEMS FOR RESEARCH

Research is needed to improve our quantitative understanding of thallium distribution in minerals and rocks. Alternate sources for the recovery of thallium metal, such as sea-floor manganese nodules and coal ash, must be delineated to cover anticipated and sudden unforeseen future demands.

Although thallium is widely distributed in the earth's crust, it is concentrated in, or has an affinity for, certain mineral species. There is evidence to suggest that its concentration in these minerals is temperature and pressure controlled. Thus, its variable abundance in specific index minerals must be studied and modeled over known mineralized deposits and rock suites of genetically different origins. It may then be possible to evaluate the potential of mineralized areas for other commodities, on the basis of the distribution and amount of thallium that is present.

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TIN

By C. L. Sainsbury and Bruce L. Reed

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ABSTRACT OF CONCLUSIONS

The United States consumes almost 30 percent of the free world's annual production of primary tin. Nearly half this amount is used in the manufacture of tinplate, principally for tin cans; the other main uses are in solders, bearing alloys, bronze, chemicals, and coatings other than tinplate. Many of these uses could be met by substitutes such as tin-free steel, aluminum, or plastics.

Current U.S. tin production, as a byproduct of molybdenum mining in Colorado, is negligible. The strategic stockpile is sufficient to guarantee against a sudden shortage of primary tin for essential uses, but at the current rate of consumption even this supply would be depleted in a little more than 4 years. Domestic reserves of tin, mainly in Alaska, would provide only about three-fourths of a year's supply, conditional resources about the same, and hypothetical and speculative resources about 2 years' supply; thus, it seems clear that the United States must continue to depend on tin imports for most of its needs. The largest foreign conditional and undiscovered resources are in southeastern Asia, Brazil, China, Bolivia, and Zaïre. The worldwide geologic association of tin with acid granitic rocks and rhyolites is so well marked that speculation as to the likelihood of finding major tin resources in new geologic environments is without redeeming value.

INTRODUCTION

Tin metal has two modifications: "white" tin of tetragonal crystal symmetry and specific gravity of 7.31, and "gray" tin of cubic symmetry and specific gravity of 5.75 (Lange, 1961). Below a temperature of 13.2°C, white tin changes to gray tin and crumbles to a powdery mass. Alloying tin with any other metal prevents this change from white to gray tin; hence, tin is seldom if ever used in pure elemental form. Tin is nontoxic, is easily melted, and has a low coefficient of friction. Although tin metal is soluble in strong acids, tin as plating is rendered

inert toward weak acids, bases, air, and other corrosive agents by the formation of a thin film of tin oxide. Probably the most important property of tin is its extreme fluidity in the molten state and thus its ability to wet many other metals and alloys. The fluidity and excellent wetting characteristics lead to its most important use as tinplate, which accounts for nearly 50 percent of the tin used in the United States.

USES

The six principal use categories of tin, in decreasing order of importance, are tinplate, solders, bearing alloys, bronze, chemicals, and coatings other than tinplate. In the highly developed countries, the principal use of tin is as a coating on steel plate for use in the manufacture of tin cans. Although aluminum, plastics, and tin-free steel (steel with a very thin coating of chromium) are capturing a large share yearly of established can production in these nations, tin is normally used in cans produced in the newly developing nations. These two factors roughly balance each other; as a result, the total yearly world consumption of tin in tinplate increases only slightly.

Because of a strong and sustained research program funded by contributions of the tin-producing nations to the Tin Research Institute (Fraser Road, Greenford, Middlesex, England), new uses of tin are established almost yearly, offsetting active trends toward the substitution of aluminum and plastics for tin. Only a few of the new uses are mentioned here; the interested reader is referred to the "Quarterly Review" of the Tin Research Institute and to the various minerals yearbooks of the U.S. Bureau of Mines.

One of the fastest growing new uses of tin is in the production of organotin chemicals. These are chemicals in which quadrivalent tin is linked to three hydrogen atoms and to an "X Group," which includes OH, Br, Cl, I, acetate, alkenyl, alkanoyloxy, or more complex derivatives. These organotin chemicals have proved to be very effective pesticides, fungicides, and wood preservatives and have relatively low toxicity. Between 1950 and 1968, production of organotin compounds rose from 50 tons to more than 10,000 tons, largely because of research initiated worldwide by the Tin Research Institute. A very rapid rise in use of organotin compounds has resulted from their use as a stabilizing agent in polyvinylchlorides (PVC). Organotins have proved effective in preventing discoloration and embrittlement of clear PVC. Because of its low toxicity, PVC stabilized with organotins may be legally used in packaging of foodstuffs.

Within the automotive industry, tin continues its long-established uses in bearings, bronzes, solders, body fillings (to smooth joins and contours), terneplate for gasoline tanks, and pewter parts. In addition, tin is being added to cast-iron or cast-steel parts to improve their machinability and is being used as an additive in sintering of iron powders. Much of the safety glass now used is made by the new technique of floating liquid glass on a molten bath of tin metal.

In keeping with the space- and nuclear-age technology, an alloy of tin and niobium has been found to be a highly superior superconductor. Such a superconductor, consisting of more than 20 km of niobium-tin ribbon wound on a wheel of 5-foot diameter, when activated in liquid helium will produce a magnetic field so strong that the entire assembly will float in space in its own magnetic field. This extreme magnetic field will be used to trap a high-energy plasma of electrons and ions produced by thermonuclear fusion. This energy source and trapping arrangement ultimately may supply unlimited quantities of cheap electric power.

Finally, mention should be made of the irreplaceable low-fusing-point eutectic alloys of tin with elements such as bismuth or antimony. These are bright, silvery, nontarnishing alloys which can be melted and remelted with negligible loss to oxide films. One such alloy, consisting of tin, bismuth, cadmium, lead, and indium, melts at 47°C. Such alloys are indispensable in automatic fire-control systems; in machining of fragile parts, which are cast in low-melting temperature alloys and machined to shape, after which the alloy is melted away; and in engineering research.

In spite of loss of some established markets, such as tin foil, new uses of tin are likely to more than offset these losses, and tin consumption is not likely to decrease in the foreseeable future.

SUPPLY

U.S. consumption of primary tin—about 57,000 tons in 1968—is about 30 percent of the free world's mine output, which in 1968 amounted to about 182,000 tons. About 90 percent of the world's tin is produced by seven countries. In 1970, Malaysia furnished 63 percent of tin imported into the United States; Thailand furnished 30 percent, and five other nations—Australia, Brazil, Indonesia, Nigeria, and the United Kingdom—combined to furnish the remaining 7 percent.

Because the United States consumes almost 30

percent of the free world's primary tin but produces virtually none, tin remains within the strategic category established by the U.S. Government. Because of this strategic category, a large stockpile of tin was accumulated by the Defense Production Administration during the 1950's. This stockpile contains a required strategic reserve of 232,000 long tons of tin. About 20,000 long tons of tin has been declared surplus from the stockpile and is gradually being disposed of by the General Services Administration.

Although tin is not produced within the United States, the strategic stockpile is sufficient to guarantee against a sudden shortage of tin for essential uses. Moreover, because the tin-producing countries are scattered widely throughout the world and across many types of political boundaries, loss of production from one area can be compensated for within a few years by increased production from other areas. Historically, tin has been available for all peace-time uses, and in fact it has often been in excess supply. Because many of the uses of tin could be met by substitutes, such as tin-free steel, lacquered cans for foods, and aluminum or plastics, tin can be considered at least partly replaceable in the world's technology.

EXPLOITATION

A discussion of tin would not be complete without mention of the fact that of all the mineral commodities in world trade, tin is unique in being regulated by international agreements, imposed by the International Tin Council. This organization is composed of members of most of the major producing and consumer countries. Producing nations contribute funds to the Council; these funds are used to create a buffer stock of tin which is disposed of or acquired by the Buffer Stock Manager, who must buy or sell tin as the world market price goes below or above predetermined prices. In times of oversupply, the Tin Council may impose production quotas which must be adhered to by the signatory producing countries .The actions of the International Tin Council serve to prevent violent price fluctuations and to insure an orderly flow of tin in the world markets. Because of the resemblance of the Tin Council to an international cartel, the United States is not a member.

Tin has been a standard metal of commerce at least since the late Bronze Age (3500–3200 B.C.). In such a long-lived world trade, diverse cultures have been brought into contact, thus modifying many of the historical cultures. For instance, the Phoenicians regularly transported tin from Cornwall (England) into world markets, the tin being furnished in large part from old alluvial placers. The bronze made from tin was used in all metal tools including weaponry for innumerable centuries. Few, if any, other metals have played such an important continuing part through the development of human civilization.

Since the beginning of historical times, tin has been available except when major wars or other political events have temporarily disrupted its usual flow. Perhaps never has tin been in jeopardy because of exhaustion of minable reserves, but political events have played the major part in all disruptions. For instance, between 1954 and 1959, production from Indonesia, the Congo, and Bolivia fell 25,000 tons, creating a shortfall which raised tin prices to an all-time high. This loss was entirely political and was alleviated by increased production in Malaysia, Thailand, and Australia. When Indonesian production is reestablished to the 1954 level, an excess of tin will be produced. In fact, Indonesian tin probably will replace some Malaysian tin, if necessary, as a result of imposition of production quotas.

New discoveries of major tin fields also have been important in maintaining world reserves. The deposits in the Congo were discovered in 1938, and reserves there must yet be largely unexplored. Within the past 10 years, the discovery and development of the Rondônian deposits in Brazil have added significantly to world production and very significantly to world reserves. After World War II, large new deposits were found in Siberia; these are sufficiently productive to satisfy the growing Soviet tin needs. To date, no major tin-bearing area of the world can be said to be totally exhausted, as proved by the reestablishment of a significant production in Cornwall, long thought of as being exhausted.

RELATION TO BYPRODUCTS

With each technological improvement in beneficiation, older deposits are returned to production, and new demands for byproducts have elevated large tonnages of tin ores from the category of resources to reserves. For instance, the tin which may ultimately be won during the mining of the Lost River fluorite-tin-tungsten-beryllium deposits in Alaska could amount to as much as 40,000 long tons of tin. Most of this tin was considered a submarginal resource until the price of fluorspar rose sufficiently to place large tonnages of rock containing tin, fluorite, tungsten, and some base metals into the reserve category. In the future, other large deposits, in which tin is only one of several valuable commodities, will undoubtedly be brought into production.

In other established mining areas, certain byproducts and coproducts have played an important part in the establishment and life of tin mines. Many placer mines produce important amounts of columbite-tantalite (Nigeria); others produce significant amounts of rare-earth minerals and thorium. Often, the economic feasibility of an operation will depend upon the byproducts. Unfortunately, such mines are subject to closure by major discoveries of deposits that contain the associated byproducts. With the discovery of the large rare-earth deposits at Mountain Pass, Calif., much of the market was lost to byproduct monazite and other minerals containing rare earths that formerly were recovered commercially from tin placers. The capture of the niobium market by pyrochlore from the Canadian deposits seriously reduced the economic potential of the placers of Nigeria, which historically had produced a salable columbite-tantalite concentrate.

In some lode deposits, cassiterite is accompanied by several valuable potential coproducts or byproducts, especially lead, zinc, silver, uranium, bismuth, cadmium, tungsten, and fluorite, but most such byproducts are not yet marketable. One advantage of complex ores, which helps offset expensive beneficiation, is that prices of all commodities are unlikely to be depressed simultaneously.

Practically all the tin recovered in North America is produced as a byproduct. The lead-zinc mine at Sullivan, British Columbia, has produced over 10,000 tons of tin as a byproduct, and some tin is recovered from the molybdenum mine at Climax, Colo. Of perhaps greater significance is the silver recovered from the complex Bolivian ores. In other mines, as at the San Antonio mine, Mexico, the silver produced has been as valuable as the tin. The large Kochiu tin fields of China were originally opened for their silver content.

In short, a certain amount of the tin produced in the world is dependent upon the value of the byproducts, but as the bulk of the tin is produced from placers with limited production of salable byproducts, it is unlikely that byproducts will greatly influence future tin production.

ENVIRONMENTAL PROBLEMS

By its nature, placer mining tends to reshape or destroy valuable lands along river courses. Without planned rehabilitation, placer tailings are useless for agriculture, but in Malaysia, dredge pools have in places been converted to fish hatcheries and fish farms. Nevertheless, in places such as the Kinta Valley, the richest tin placers lie beneath the most productive farmlands. In such areas, land-use planning far ahead of current operations is required for extraction of the tin. In other areas, such as Bolivia, lode mines are in lands virtually useless for agriculture. That development of new lode mines need not interfere with other land uses is illustrated by the successful reopening of the South Crofty mine in Cornwall, England, certainly one of the most scenic areas on earth.

As noted by Heindl (1970, p. 767), "Industrial tin operations, because of the relatively high unit value of the product and the size of the operations, are not important contributors to industrial pollution. Primary tin-smelting operations discharge SO_2-containing gas from a 250-foot stack." At present, no tin smelters are in operation in the United States, and no smelter-gas problem from tin ores exists.

In Southeast Asia, where the greatest tin reserves and resources are found, many of the tin placers are beneath sea water, and no conflicting land-use problems exist. The same can be said for the Siberian placers beneath the Arctic tundra. At present, there is little likelihood that land-use conflicts or environmental issues can seriously curtail world tin production.

GEOLOGIC ENVIRONMENT

GEOCHEMISTRY[1]

Tin is an element of atomic number 50 and atomic weight 118.70, consisting of the isotopes, in percent, Sn^{112}, 0.95; Sn^{114}, 0.65; Sn^{115}, 0.34; Sn^{116}, 14.24; Sn^{117}, 7.57; Sn^{118}, 24.01; Sn^{119}, 8.58; Sn^{120}, 32.97; Sn^{122}, 4.71; and Sn^{124}, 5.98—one of the more complex isotopic compositions known. Tin has two common valences, +2 and +4, with ionic radii respectively of 0.93 A and 0.71 A. Table 132, modified from Borchert and Dybek (1960), shows the ionic radii and electronegativity of the more common ions with which tin is associated. Tin also is amphoteric, forming either acids or bases. Because of its similarity

TABLE 132.—*Ionic radii and electronegativity of ions similar to* Sn^{2+} *and* Sn^{4+}

Ion	Ionic radius (i)	Electronegativity (e)	$i \times e$
Sn^{2+}	0.93	1.65	1.535
Ca^{2+}	.99	1.00	.99
Cd^{2+}	.97	1.50	1.47
Fe^{2+}	.83	1.65	1.37
Sn^{4+}	.71	1.80	1.33
Ti^{4+}	.68	1.60	1.088
Fe^{3+}	.67	1.80	1.206
Mg^{2+}	.78	1.20	.936
Sc^{3+}	.83	1.30	1.079

[1] Modified from a statement prepared by Michael Fleischer, U.S. Geological Survey.

to other common metallic ions, tin may proxy for these ions in common minerals or may form tin analogs of common minerals. Thus tin may be dispersed in minerals containing iron, titanium, or calcium—for example, in biotite (up to several hundred parts per million), rutile (900 ppm), or andradite garnet (up to 1.7 percent). A good example of a tin analog is the mineral malayaite ($CaSnSiO_5$), in which tin replaces titanium in the mineral sphene. Malayaite is found in contact-metamorphic skarns (El Sharkawi, 1966). It has long been known that magnetite from skarns near tin deposits commonly contains tin in anomalous amounts, and recently Desborough and Sainsbury (1970) showed that cassiterite from the Lost River tin deposits, Alaska, has exsolved from magnetite. Thus the iron-tin association is well established.

The crustal abundance of tin is in the range of 2–3 ppm (parts per million). Work by several investigators on meteorites (Goldschmidt and Peters, 1933; Onishi and Sandell, 1957; Borchert and Dybek, 1960) has shown that the nickel-iron phase contains an average of 100 ppm tin, whereas the chondritic phase contains about 5 ppm and the troilite phase about 15 ppm. This suggests that a primary enrichment occurred in the nickel-iron phase in the earth's core. During the magmatic differentiation of the crust, tin is progressively concentrated in the more acid differentiates, as shown in table 133.

TABLE 133.—*Range and average contents of tin in various materials*

[Values in parts per million except where noted]

Material	Usual range reported	Average
Igneous rocks		
Ultramafic rocks	0.1–1.3	0.6
Basaltic rocks	0–8	1.1
Intermediate rocks	0–10	1.4
Silicic rocks	<1–15	3.5
Greisens	780–7,800	------
Alkalic rocks	8–39	------
Sedimentary rocks		
Limestones	---------	0.2?
Sandstones	---------	.4?
Shales and clays	1–20	6
Soils	Mostly-- 0–10	8?
Phosphorite	0–15	------
Other materials		
Ground waters	parts per billion-- 0–30	<1
Oceans	do---- 0.3–1.2	------
Hot springs	do---- 0.1–1	------
Air, urban areas	nanograms/cu m-- 3–300	------

Within sedimentary rocks, the amount and distribution of tin is imperfectly known, although some shales may contain as much tin as tin-rich granites (table 133). However, no sedimentary rocks are known that are enriched in tin to such a degree as to approach commercial ore.

Of all the metals found in epigenetic deposits, tin shows perhaps the most clear-cut relation to a single rock type—almost all primary tin lodes are associated with biotite or biotite-muscovite granites, or their extrusive equivalents. This imposes certain parameters on rampant speculation about the genesis of tin deposits. Whatever the genesis, it has something to do with geochemical, physicochemical, or petrochemical processes that are peculiar to granites. This is discussed briefly in the later section on genesis.

GEOCHEMICAL CYCLE

The knowledge of the geochemistry of tin is based largely on comparison of different types of analyses of different rocks and different types of deposits, from widely dispersed areas of the world. Before the geochemical cycle of tin can be understood fully, many more studies on complete rock suites, ores, and minerals from single districts are needed. The work of Butler (1953) in Cornwall is valuable in tracing tin through the weathering cycle. Data have been assembled, but only in preliminary form, from the Lost River area, Alaska (Sainsbury and others, 1968), and are summarized in figure 71. (For detailed descriptions of the tin deposits and regional geologic setting, see Knopf, 1908, and Sainsbury, 1964b and 1969.) This tin-bearing area is typical of the sulfide-cassiterite type of high-temperature deposit, but unusual in that it includes large deposits of fluorite, containing beryllium in economic amounts which are zoned about the tin deposits.

Several significant observations should be made about figure 71: (1) Tin is greatly concentrated in the granites relative to the limestone and shale through which the granites penetrated. (2) The heavy-mineral fraction of the granite unquestionably is the clearest indicator of associated tin deposits, although the biotite also contains a high amount of tin. (3) Tin is slightly concentrated in the hornfels zones around the granite, and is highly concentrated in all the individual minerals separated from the tin and beryllium lodes, clearly recording a common genesis. (4) Soils (over limestone) are greatly enriched in tin over the ore deposits, and the tundra plants over ore bodies clearly are enriched in tin. (5) Bulk stream sediments are enriched in tin downstream from tin deposits. (Water was not analyzed.)

More studies, and in greater detail, of this type are needed to establish criteria required for making valid geochemical comparisons in diverse areas of

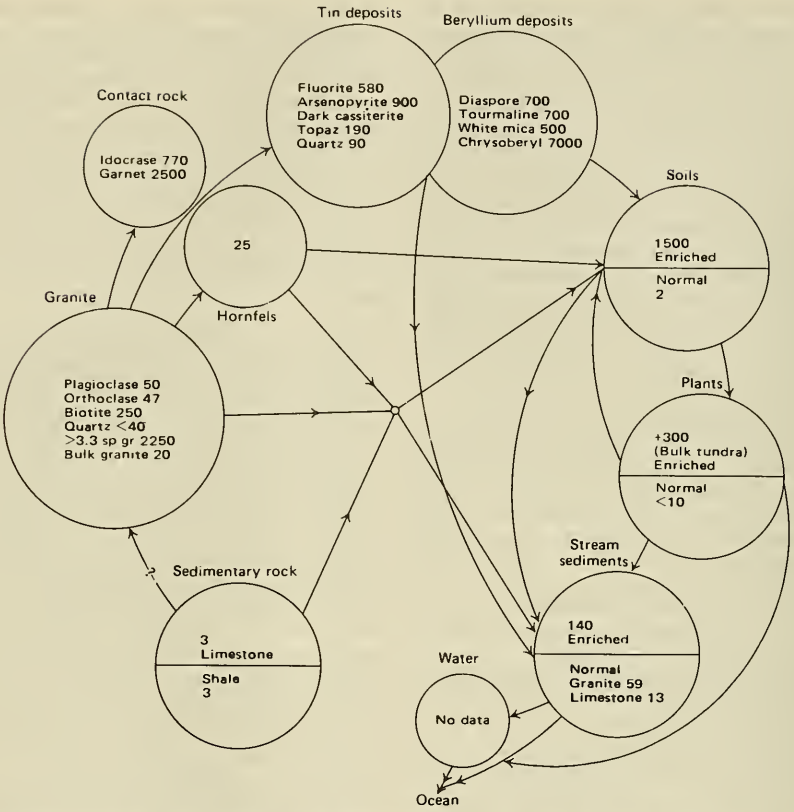

FIGURE 71.—Geochemical cycle of tin, western Seward Peninsula, Alaska. Number indicates maximum concentration, in parts per million. For granite the concentration is the average of five samples: for individual minerals in granite it is the average of three samples. In plants, the concentrations vary with plant type; value shown is the maximum observed gain over the corresponding soil. (From Sainsbury, Hamilton, and Huffman, 1968, pl. 2.)

the world and for formulating dependable exploration techniques. In another area near the Lost River district, where cassiterite in placers is associated with quartz-cassiterite veins not accompanied by sulfides, bulk stream sediments were devoid of geochemical anomalies, even though overlying a buried placer. Only panned concentrates revealed the presence of the lodes (Sainsbury and others, 1970).

TIN MINERALS

Cassiterite (SnO_2) contributes almost all the tin of industry, although small amounts are recovered from tin-sulfide minerals, such as stannite, cylindrite, and teallite. The more common tin minerals are listed in table 134. This list is restricted to tin minerals containing oxygen or sulfur; tin also forms

TABLE 134.—*The more common tin minerals*

Name	Composition	Geographic occurrence
Argyrodite	Ag_8GeSn_6	Bolivia.
Arandisite	Complex tin silicate	South West Africa.
Berndtite	Beta SnS_2	Do.
Cassiterite	SnO_2	Worldwide.
Canfieldite	Ag_8SnS_6	Bolivia, Tasmania.
Colusite	$Cu_3(As,Sn,V,Fe,Te)S_4$	Montana.
Cylindrite	$Pb_3Sn_4Sb_2S_{14}$	Bolivia, Tasmania.
Franckeite	$Pb_5Sn_3Sb_2S_{14}$	Do.

TABLE 134.—*The more common tin minerals*—Continued

Name	Composition	Geographic occurrence
Herzenbergite	SnS	Bolivia.
Hielmite	Y,Fe,Mn,Ca,Sn-niobate	Sweden.
Hochschildite	$PbSnO_3 \cdot nH_2O$	Bolivia.
Hulsite	$12(Fe,Mg)O \cdot 2Fe_2O_3 \cdot 1SnO_2 \cdot 3B_2O_3 \cdot 2H_2O$.	Alaska.
Malayaite	$CaSnSiO_5$	Malaya, Cornwall.
Mawsonite	$Cu_{14.5}Fe_{12.5}Sn_{10.4}S_{33}$	Tasmania.
Native tin	Sn	New South Wales.
Nigerite	Complex tin silicate	South West Africa.
Nordenskioldine	$Ca,Sn(BO_3)_2$	Norway, South West Africa.
Ottemannite	Sn_2S_3	Bolivia.
Paigeite	$30FeO \cdot 5Fe_2O_3 \cdot 1SnO_2 \cdot 6B_2O_3 \cdot 5H_2O$.	Alaska.
Renierite	$Cu_3(Ge,Fe,Sn,Zn)S_4$	(?)
Sorensenite	$Na_2SnBe_2Si_6O_{16}(OH)_4$	Greenland.
Stannite	Cu_2FeSnS_4	Worldwide.
Stokesite	$Ca,Sn(Si_3O_9) \cdot 2H_2O$	Cornwall.
Sukulaite	$Ta_2Sn_2O_7$	Norway.
Teallite	$PbSnS_2$	Bolivia.
Thoreaulith	$SnTa_2O_7$	Congo.
Varlamoffite	H_2SnO_3	Do.

compounds with tellurium and selenium, but only at high temperatures and pressures, and no such minerals are known to occur in nature. Only in Bolivia are many of the sulfide minerals present in sufficient amounts to be recovered, and their recovery requires a complex hydrometallurgical treatment. Stannite is found in many tin-sulfide deposits, and small amounts are recovered. Of all the coproducts or byproducts produced, tungsten is probably the most important.

TYPES OF DEPOSITS

Tin is produced from six different types of lode deposits, and from placer deposits.

LODE DEPOSITS

Lode tin deposits can be classified into six distinct types, following the classification of Ahlfeld (1958): (1) pegmatite deposits, (2) pneumatolytic-hydrothermal deposits, (3) subvolcanic or tin-silver deposits, (4) disseminated deposits, (5) contact-metamorphic deposits, and (6) fumarole deposits.

PEGMATITE DEPOSITS

Tin-bearing pegmatites are generally associated with granitic rocks and contain cassiterite (SnO_2), as well as other uncommon, valuable minerals such as columbite-tantalite, beryl, or spodumene. Most productive pegmatites are in areas of deep tropical weathering, which permits the economic exploitation of pegmatites that contain less than 0.4 percent tin. Some pegmatites are very large, contain cassiterite throughout, and constitute major reserves of tin; one example is the Manono pegmatite in the Democratic Republic of the Congo, which is 10 kilometers long and 100–400 meters wide.

PNEUMATOLYTIC-HYDROTHERMAL DEPOSITS

Most of the major lode tin deposits of the world (those of Bolivia excepted) are of the pneumatolytic- hydrothermal type. (This distinction of the Bolivian type of deposit from what may be called the Cornwall type may not be valid. The authors here are following most other workers, who consider them in separate categories.) Lodes are near or in biotite or two-mica granite and form replacement deposits or fissure fillings in diverse types of country rock. Owing to a regional zonation commonly displayed, deposits vary widely in mineralogy. In or near granite, lodes typically contain cassiterite in greisen (quartz-mica rock) or quartz-topaz-tourmaline rock that also contains wolframite and many base-metal sulfides. Farther from the granite, some lodes contain stannite (Cu_2FeSnS_4), base-metal sulfides, and silver; in some places, the deposit may be valued principally for the silver content. Some individual deposits are very large, such as the Dalcoath lode in Cornwall, England, which produced 80,000 tons of tin (Dines, 1956).

SUBVOLCANIC OR TIN-SILVER DEPOSITS

The subvolcanic or tin-silver type of deposit is exemplified by the mineralogically complex and very rich deposits of Bolivia, where bonanza tin lodes also contain large amounts of silver. Deposition in a near-surface environment led to strong telescoping of the deposits and to mineralogical complexity, which creates a problem in the recovery of tin. Rare tin-bearing minerals, such as teallite, herzenbergite, cylindrite, and canfieldite, are common in these deposits. Individual mines in such deposits have produced enormous amounts of tin; one mine at Llallagua, Bolivia, produced over 500,000 tons (Ahlfeld, 1936).

DISSEMINATED DEPOSITS

In these deposits, cassiterite in small amounts is disseminated widely in altered granite, especially in border zones or parts changed by addition of tourmaline, topaz, or fluorite. Although only a few disseminated deposits are worked commercially at present, erosion of such lodes (particularly border zones of granites) has resulted in large and rich placer deposits (Southeast Asia and elsewhere).

CONTACT-METAMORPHIC DEPOSITS

Contact-metamorphic deposits are fairly uncom-

mon and generally consist of cassiterite or malayaite in tactites near granite (Cornwall). The minerals customarily associated are magnetite, garnet, pyroxene, fluorite, tourmaline, various sulfide minerals, and, in the Lost River area, Alaska, beryllium minerals (Sainsbury, 1964a). The grade is generally less than 0.5 percent tin, but large tonnages and potential byproduct recovery of base metals, beryllium, and fluorite may give added importance to such deposits when other tin supplies dwindle.

FUMAROLE DEPOSITS

The term "fumarole deposits" was used by Ahlfeld (1958) to describe small but widespread deposits that form fracture fillings in Tertiary lavas. The fracture fillings contain cassiterite generally intergrown with specular hematite, and minute grains of cassiterite are distributed in kaolinized wall rock along veins. A few deposits are mined commercially, on a small scale. Placers derived from the erosion of such veins are mined in Mexico, New Mexico, and Argentina.

PLACER DEPOSITS

Worldwide, placer deposits are more productive and more cheaply mined than lode deposits; they furnish, therefore, most of the commercial production. Cassiterite, the main tin mineral of commerce, is both heavy and chemically resistant; consequently, it forms large placers or residual concentrations. Placers can be conveniently classed as residual, eluvial (slope), alluvial (stream), marine, and fossil placers.

RESIDUAL PLACERS

Residual placers form in place over a bedrock source of cassiterite by the chemical decay and removal of the rock minerals. At places, such as Kitololo in the Democratic Republic of the Congo, residual placers grade downward into weathered lodes and are mined either as placers or as open-pit lodes. In a truly residual placer, the enriched zone contains not only heavy minerals such as cassiterite and columbite-tantalite but also chemically resistant light minerals such as beryl. In Indonesia, residual placers commonly are cemented tightly by hydrous iron oxides, forming the "kaksa" of industry, which must be crushed to free the cassiterite.

ELUVIAL (SLOPE) PLACERS

Eluvial placers are formed by the chemical decay of tin-bearing rocks and the gravity separation of cassiterite and other heavy resistates as the decayed mantle moves downslope under the influence of sheetwash, gravity, and, locally, frost action. Such placers grade imperceptibly into residual placers upslope, and often into alluvial (stream) placers downslope. Because of active gravity sorting, some eluvial placers are richer than residual placers; many, however, contain coarse rubble, and, in cold regions (Alaska and Siberia), fragments of unoxidized deleterious constituents such as arsenopyrite.

ALLUVIAL (STREAM) PLACERS

Alluvial placers, by far the largest and richest placers, furnish most commercial tin. In 1964, almost 60 percent of the world's tin production came from alluvial placers in Southeast Asia (Shelton, 1965). Other major producing placer areas are in Nigeria and in the newly developed tin fields in the Territory of Rondônia, Brazil (Brazil Div. Fomento Prod. Mineral, 1964). Alluvial placers occupy both modern and fossil streambeds, and the distribution of tin is dependent upon the location of the source areas and the hydraulics of running water. The best placers are formed near lodes in sections of streams where the velocity is sufficient to result in good gravity separation but not enough so that the channel is swept clean. A type of location proved to be especially favorable for placer tin is a long stream that flows parallel to the margin of a tin-bearing granite.

In Southeast Asia, stream placers formed seaward of present shorelines when sea level was eustatically lowered periodically during the Pleistocene. These stream placers now lie beneath sea water; they are mined by seagoing dredges. In Rondônia, Brazil, some placers lie in areas so low that sea water covered them during certain interglacial periods when sea level stood much higher than at present. Elsewhere in the world, as in Cornwall and Tasmania, both lode and placer deposits occur within areas which have fluctuated between land and sea bottom during Pleistocene climatic changes; placers in such areas may have characteristics of both marine and alluvial deposits.

Owing to the long exposure to air and water and to good gravity separation, tin concentrates produced from alluvial placers are relatively free of deleterious constituents and may contain as much as 70 percent tin; as such, they constitute prime smelter concentrates.

MARINE PLACERS

Most marine placers are beach placers or inundated beach placers. They form where a marine shoreline intersects or transgresses either a stream valley containing alluvial cassiterite or a bedrock source of tin. Although a true beach placer norm-

ally has a large length-to-width ratio, a placer of transgressive origin may consist of a sheet of heavy minerals buried beneath marine sediments (Australia). Placers of this type have yielded large amounts of cassiterite in Indonesia (Bangka and Billiton Islands) and will continue to do so.

FOSSIL PLACERS

Any or all of the preceding four types of placers may become fossil placers by burial beneath younger sediments or lava. Uplift and renewed erosion along disrupted drainages may expose such placers irregularly, and second-cycle alluvial placers may be generated (Nigeria). Depending in part on the geologic age, the gravels of some fossil placers may be lithified to such an extent that they must be mined by lode-mining methods. In others, major postdepositional changes, such as partial solution of cassiterite, may affect the value.

RESOURCES

IDENTIFIED RESOURCES

Tin resources of the world were computed by Robertson (1965); his figures were incorporated with some modifications and additions into a report by Sainsbury (1969). These two reports contain the facts and presumptions of the calculations of reserves and brief descriptions of the main tin-producing deposits of the world.

In the present report, new calculations have been made, principally to accommodate this volume's classification of undiscovered resources in both known and unknown districts. Such geologic calculations require a bold and optimistic approach, and new figures are presented herein (table 135). Factors which can be used to estimate undiscovered resources are largely geologic and partly intuitive and include:

1. History of production.
2. Rapid rise of reserve figures in newly discovered districts, such as Rondônia, in Brazil.
3. Potential favorability of parts of the world in which even basic geologic mapping is lacking.
4. Unexpected new developments in old districts, such as the major ore bodies opened recently in Cornwall.
5. Comparison of tonnages mined in countries having a long production history, such as Malaysia, with other countries having a substantial production but with higher grade known reserves, such as Indonesia and Thailand.

When these factors are applied optimistically, the potential resources of tin in undiscovered districts seem to be large, and reserves and resources in known districts are increased substantially over the previous estimates by Robertson (1965) and Sainsbury (1969).

The tin reserves and resources of China, Russia, and other Communist countries cannot be assessed accurately from published data. Even the International Tin Council has not attempted a tabular summary. For this report, however, we have estimated the magnitude of tin reserves and resources of China and Russia.

As can be seen from table 135, all the identified tin resources lie within the established tin-producing countries. The figures given for these resources do not differ greatly from those of the previous resource calculations mentioned above. In this report, inferred reserves for countries with revived mining of substantial amounts of tin, such as England or Australia, are assumed to be equal to or greater than their measured and indicated reserves. In other countries, such as Zaïre (the Congo) and Thailand, inferred reserves must be much greater than the figures for measured and indicated ore.

Probably the greatest departure from earlier reserve estimates is the assignment of substantial proved and inferred reserves for England and Australia and greater inferred reserves for Indonesia and Thailand. The greater inferred reserves for Indonesia and Thailand are based directly upon a comparison of grade of material being mined by dredges. Inasmuch as the tin-producing areas in Thailand, Malaysia, and Indonesia are roughly comparable in size, a large amount of tin will no doubt be mined in Thailand and Indonesia before the grade of their alluvial deposits drops to that being mined today in Malaysia.

Because classes of reserves in this report differ from those in all previous reports, no direct comparison can be made beyond the figures for identified resources, which roughly correspond to the total in categories historically called measured, indicated, and inferred.

HYPOTHETICAL RESOURCES

Evaluation of hypothetical resources can be based in part on the past mining history of an area. Countries such as Malaysia and Indonesia, which have produced large amounts of tin for nearly a hundred years and which can expand their production greatly if a slight price increase and an adequate market warrant, are going to continue to produce tin for nearly as long as they have already done. Other countries, such as Nigeria, have well-known limiting factors which suggest that they may not be able to produce for extended periods of time. Hence, their subeconomic resources must be smaller.

TABLE 135.—*Tin reserves and resources of the world, in long tons of tin metal*

Reserves: Identified deposits from which minerals can be extracted profitably with existing technology and under present economic conditions.
Conditional resources: Specific, identified mineral deposits whose contained minerals are not profitably recoverable with existing technology and economic conditions.
Hypothetical resources: Undiscovered mineral deposits, whether of recoverable or subeconomic grade, that are geologically predictable as existing in known districts.
Speculative resources: Undiscovered mineral deposits, whether of recoverable or subeconomic grade, that may exist in unknown districts or in unrecognized or unconventional form.

Country	Reserves		Conditional resources		Undiscovered resources	
	Measured plus indicated	Inferred	Paramarginal	Submarginal	Hypothetical	Speculative
North America:						
U.S.A.	8,435	33,100	----------	43,000	40,000	70,000
Canada	10,000	10,000	14,000	14,000	----------	200,000
Mexico	1,000	5,000	----------	----------	----------	47,700
Total	19,435	48,100	14,000	57,000	40,000	317,700
South America:						
Bolivia	485,000	500,000	----------	500,000	1,250,000	----------
Brazil	300,000	300,000	1,074,000	----------	1,674,000	1,000,000
Argentina	3,000	3,000	----------	----------	----------	7,000
Total	788,000	803,000	1,074,000	500,000	2,924,000	1,007,000
Europe:						
England	128,700	128,700	----------	600.000	425,000	----------
Spain and Portugal	15,000	15,000	----------	150,000	750,000	----------
France	----------	4,000	----------	4,000	----------	----------
Total	143,700	147,700	----------	754,000	1,175,000	----------
Asia, Non-Communist:						
Indonesia [1]	500,000	1,860,000	540,000	540,000	----------	----------
Malaysia	600,000	230,000	----------	1,000,000	1,500,000	1,000,000
Thailand [2]	217,000	1,000,000	1,860,000	----------	1,500,000	1,000,000
Burma	250,000	250,000	----------	----------	250,000	250,000
Other countries	17,500	90,000	----------	----------	----------	100,000
Total	1,584,500	3,430,000	2,400,000	1,540,000	3,250,000	2,350,000
Africa:						
Nigeria	138,000	138,000	----------	100,000	[3] 500,000	----------
Zaire	65,000	130,000	1,000,000	----------	----------	1,000,000
Other countries [4]	117,000	117,000	----------	22,000	----------	330,000
Total	320,000	385,000	1,000,000	122,000	500,000	1,330,000
Australia and Tasmania	94,330	94,000	100,000	100,000	100,000	500,000
China [5]	500,000	1,000,000	1,000,000	1,000,000	1,000,000	1,000,000
U.S.S.R. [5]	200,000	420,000	300,000	300,000	300,000	1,000,000
World total	3,649,965	6,327,800	5,888,000	4,373,000	9,289,000	7,504,700

[1] Inferred reserves in Indonesia are greatly expanded over the estimate of Sainsbury (1969) on the basis of grade of placer deposits being dredged currently in Malaysia and Indonesia. Present grade of Indonesia dredge ground is about 0.62 lbs per cu yd, somewhat higher than that dredged in Malaysia in 1947. Hence, before grade in Indonesian placers falls to the level of current grades in Malaysia, as much tin will be produced from Indonesian placers as was produced in Malaysia between 1937 and 1971, or about 1,860,000 long tons.

[2] The same computation used for Indonesia was applied for Thailand on the assumption that the stanniferous areas were equal to those of Malaysia.

[3] In old channels buried under volcanic rocks.

[4] Republic of South Africa, South West Africa, Southern Rhodesia, Cameroons, Burundi-Urundi, and the north African countries.

[5] These are classed as no better than educated guesses.

SPECULATIVE RESOURCES

In assessing the possibility of finding new districts, several factors unique to tin must be considered. These are:

1. Tin has been mined and used throughout the world for thousands of years, and whatever major tin deposits exist in regions settled or penetrated by civilized peoples have probably been discovered. Conversely, entire new districts might still be found in remoter regions, as attested by the recent discovery of a major district (Rondônia) in western Brazil.
2. Each discovery of new tin deposits merely reinforces the fact that deposits containing economic amounts of tin are invariably similar to those deposits which have been mined for thousands of years. One cannot, therefore, even validly speculate that new types of deposits will be found for tin, such as have been found recently for beryllium (Spor Mountain, Utah; Lost River, Alaska) or for gold (Carlin and Cortez, Nev.).
3. Many of the great mining districts of the world were found by Cornish miners who left Cornwall after her mining industry collapsed, and who migrated all over the world. In their search for gold, diamonds, or base metals, these miners are unlikely to have overlooked major

tin deposits in areas they penetrated.

4. Finally, with the possible exception of commercial deposits of chromite, tin displays such a well-marked geologic association—with acid granitic rocks or rhyolite—that speculation as to the finding of major tin reserves and resources in entirely new geologic environments is without any redeeming value; it is like speculation as to the possibility of the seventh dimension, and the planning of structures based upon the speculative existence of it.

In assembling the table of undiscovered resources, it has been assumed that but a few new tin deposits will be found. For instance, the estimate of U.S. resources includes the assumption that tin deposits may be found on the Aleutian Islands, whose geology is roughly comparable to the Japanese Islands, which have produced moderate amounts of lode tin. Some tin deposits may be found in the southern Alaska Range, where placer tin has long been known and where Reed and Elliot (1970) have found tin anomalies in stream sediments near biotite granites. Analyses of placer concentrates collected between 1900 and 1954 from many Alaskan streams have shown that noteworthy tin occurs in numerous localities where tin deposits are not known (J. C. Hamilton, written commun., 1972). Tin-bearing lodes may be found, but no major new districts are believed likely to exist near such areas. In Canada, perhaps a few more mines similar to the Sullivan will be found, as will be more mines similar to the Mount Pleasant in eastern Canada. But speculation about the finding of large reserves in North America faces one rigid fact—there are no known large tin deposits, lode or placer, even in areas with favorable rock types. Again, most of these areas have been panned by the gold seekers.

On the basis of the above factors, one cannot reasonably expect to find speculative resources of any magnitude in the United States, and areas favorable for new deposits in North America are virtually limited to areas such as the Canadian Shield or the rhyolite areas of Mexico. Such deposits likely will be small.

In South America, areas may remain in Rondônia, possibly even in easternmost Bolivia, in which many new deposits similar to those now known may be found. This leads to large speculative resources in South America. Inasmuch as the large Rondônian deposits occur in and near Precambrian granites, one can speculate that the Precambrian Shield areas in the Guianas and eastern Colombia may also contain tin deposits. Perhaps a field even as large as the Nigerian tin fields could exist there. Elsewhere in South America, speculative placer resources in Bolivia would exist near some lode tin deposits and hypothetical resources would be in deeper, unknown ore bodies in known districts.

In Europe, there is little likelihood for the discovery of large new districts. However, it is assumed that at least 10 more Wheal Jones, or South Croftys, will ultimately be found in the old established Cornish mining district. In Spain and Portugal, because of the favorable geology, the known deposits, and the archaic state of mining and exploration, large amounts of tin are assumed to remain in unknown deposits. Nowhere else in Europe can one postulate substantial tin resources, even in the Erzgebirge, because the intensive exploration and mining by the Germans during World War II have exhausted that possibility.

In Asia, the long history of mining, the great extent of the placer deposits, and the remoteness of much of the jungle country probably insure that new lode and placer deposits will be found. Large reserves undoubtedly lie offshore on the Sunda Shelf and ultimately will be found and mined. Tin will be found in Burma, perhaps mostly associated with tungsten deposits, but most of this tin will be in the known tin belt.

Because of the remoteness, the jungle cover, and the relative recency of the discovery of the tin fields of Zaïre, both sufficient area and favorable geology indicate the possibility for discovery of another tin field the size of the Nigerian field. In northern Africa, the scattered known deposits, associated with biotite granite, the remoteness of the area, and the poor state of geologic knowledge all suggest that tin deposits may be found there.

In Australia, the rapid resurgence of tin mining since 1965 proves that new deposits will be found, principally in Tasmania and possibly in Western Australia.

In Communist China, it is assumed that new deposits will be found in the remote ranges of the Himalayas, as well as in known districts, when modern mining and exploration techniques become available, but elsewhere in China the long occupancy by civilized people who have used tin suggests that major new districts probably will not be found.

In the U.S.S.R., tin deposits not yet known probably exist in the tundra-covered areas of Siberia and in the Magadan area of eastern Siberia, for numerous deposits have been found in these areas since World War II. Despite the large number of Soviet geologists actively employed in economic geology, it is unlikely that Asiatic Russia has yet been adequately explored, though it is unlikely, too,

that large new tin districts will be found.

Resources which may exist in Antarctica and Greenland are not considered because data on which to base realistic evaluations are not available.

The grand total of all the reserves and resources listed above is about 37 million long tons of tin. This is sufficient to sustain a world consumption of 200,000 long tons of tin per year for about 185 years.

PROSPECTING TECHNIQUES

Before discussing the methods used in searching for tin deposits, the authors would like to repeat two statements made by K. F. G. Hosking at the First International Symposium on Tin, in London, in 1967 (Hosking, 1967, p. 269).

> Sound prospecting programmes designed to locate new primary tin deposits are usually based, to no small degree, on the designers' views concerning the relationship between such deposits and granitic rocks.
>
> * * * * *
>
> As far as possible the writer has refrained from discussing those questions of relationship which require consideration of the sources of granite magmas, granitising agents and ore-forming ones, and theories of the nature of these agents and of the chemistry of ore genesis. He has adopted this line of action because he believes that a good exploration program must be based essentially on facts, and that a program founded largely on theoretical concepts, however sophisticated the latter may appear to be, is little better than one which requires only that a blind-folded person should stick a pin in a map in order to find a tin deposit.

Following somewhat along the lines above quoted, the authors are here confining their discussion to the accepted exploration techniques. These techniques are based in part on application of concepts that were originally theoretical but have been "stabilized" by a long history of facts.

In regional exploration, analyses of major tectonic and petrologic features are of great value. Because of the obvious relation of all known tin deposits to acid granitic rocks, tectonic elements that localize such granitic rocks are considered; these elements vary from major mountain ranges with granitic cores, subjacent volcanic rocks, and extrusive rhyolites to isolated stocks and bosses of proper composition. Certain factors may then be evaluated for localizing favorable ground within the larger elements; these factors may be grouped under two broad categories: tectonic and geochemical.

Numerous authors have noted that the apical parts of granitic masses, as well as the margins, are especially favorable for the occurrence of tin deposits. Hosking (1967, 1969, 1972) holds that these apical parts, which he calls "cusps," are of great, almost overriding, importance in localizing tin deposits. Other authors (Stemprok, 1967; Sainsbury, 1969; Dines, 1956) are inclined to consider that postgranite fractures of both regional and local extent are of great importance in localizing the larger and richer lode ore shoots of some of the world's tin districts. When one studies the descriptions of the great lode mining districts of the world, one cannot escape the conclusion that most rich veins are localized along fractures which formed long after the consolidation of the enclosing granite. Where great tin lodes are mined within great expanses of granite, such as in Cornwall, in veins that (1) conform to regional fracture patterns which cut the granites, and (2) may lie entirely blind thousands of feet below the present surface (which itself is an unknown distance below the original apical part of the granites) as at South Crofty mine in Cornwall, then it is extremely difficult to relate the tin to "cusps" (cupolas?) on the original surface of the granite. Even Hosking himself pointed out that regional fracture patterns have localized deposits in Cornwall (Hosking, 1967, p. 297).

The margins of granites, however, have been proved to be especially favorable places for the occurrence of placer deposits, especially where streams have followed long distances along such margins. Stemprok (1967) showed that margins of granitic rocks in the Erzgebirge in Czechoslovakia are enriched in tin, and he related this enrichment to the escape of volatiles from deeper parts of the granite mass along joints and fractures in the shell of the granite. Sainsbury (1964b) has shown that even though the main tin-tungsten-beryllium-fluorite lode at Lost River, Alaska, lies generally above the apex of the granite (thus supporting Hosking's views), the main tin lodes are along faulted dikes intruded along faults of a regional set which cut the granites and postdate them by an appreciable time. An enrichment of tin in the marginal shell of the granite is related to small veinlets localized in the cooling joints of the granite. Again, Štemprok and Šulcek (1969) have shown that tin-bearing granites in the Krušné hory Mountains of Czechoslovakia have marked alteration along flat-lying zones at great depths in the granite. The Bolivian deposits are localized near subjacent porphyry intrusions, but they lie along veins that pass downward out of and beyond some of the porphyry intrusives.

A reasonable conclusion is that tin deposits of large tonnage and low grade may be directly related to the "bleeding off" of volatiles above cupolas ("cusps") of granites or along the fractured regions of such intrusives but that the large and rich veins

are localized in faults and fractures that postdate the intrusives and may or may not have any relationship to "cusps."

Hence, in regional exploration of granitic terranes, a study of the major fracture patterns is invaluable. It is especially valuable to determine whether regional faults or fractures followed the intrusion of the granites closely enough in time to allow for the cooling of the shells of the intrusives, entrapment of volatile elements in deeper parts of the granites, and then rupture of these deep parts by major fractures while volatiles were still able to escape at high temperature.

Once a favorable granitic terrane is recognized, can one use the petrogenic characteristics of the granites to give a dependable clue as to whether tin deposits are likely to be associated? The literature upon this subject is voluminous and in large part contradictory. For a good discussion, see Hosking (1967), who rather effectively showed that to date the only infallible indication of a granite that is favorable for tin deposits is the known presence of tin deposits! On the other hand, Beus (1969, p. 70) has shown, by a statistical treatment of data obtained by analyses of both bulk granite and biotite, that statistically significant variations are found between granites of nonstanniferous regions and granites of stanniferous regions, as well as between biotites from such granites, in certain areas in Russia. Beus' figures show that 98 percent of samples from granites of nontin-bearing provinces must contain less than 10 ppm tin, whereas only 12 percent of samples from granites of stanniferous areas contain less than 10 ppm tin. However, we must still face the fact that the determination that a granite (or granites) contains a high amount of tin (more than 100 ppm) is still no guarantee that a single workable tin lode will be found in or near that granite.

A further problem encountered in the search for tin deposits using the geochemical and petrologic features of granites is that the analytical methods used by different workers are not directly comparable and give wide variations in tin values for a single rock, and that the degree of freshness, possible deuteric alteration, and classification of the rocks investigated are seldom standardized by scouting of several workers.

Following a suggestion at the First International Technical Conference on Tin in London in 1967, and after additional discussion at the Second International Technical Conference on Tin in Bangkok in 1969, a cooperative program was set up to have analyses and petrologic descriptions made of the same granites (in fact, sawed slabs of a single large piece of granite were to be used in the laboratories) to determine just how many variations would be found. Results obtained to date show that analyses and study by three different geological surveys have resulted in wide variations in tin content, as well as different classifications, for identical pieces of two Alaskan tin-granites. Results of continuing studies will be reported in an International Symposium to be held in Europe in 1974 (Dr. Miroslav Štemprok, Ustredni Ustav Geologicky, Malostranske Nam 19, Praha, Czechoslovakia).

In the geochemical prospecting of an area presumed to contain tin deposits, the standard techniques of panning of stream gravels and collection of stream sediments are used—and this cannot be overemphasized—but they do not always give comparable results! Because cassiterite, the main ore mineral of tin, is both heavy and chemically stable in the surface environment, panned concentrates from streams are a necessity in searching for tin deposits. Near the nonsulfide types of tin deposits no geochemical anomalies will be found in stream sediments, especially in the finer grained fraction. Varlamoff (1969) has shown that in the Congo only panned concentrates will reveal tin anomalies. Brundin (1969) has shown that in geochemical prospecting in Sweden, in glaciated areas, heavy-mineral concentrates were necessary in searching for deposits containing scheelite, cassiterite, and wolframite, and also served in finding ores of sulfide minerals containing base metals. Sainsbury, Hudson, Kachadoorian, and Richards (1970) documented an area in Alaska where a stream-sediment survey using —80 mesh or —40 mesh fractions of total stream sediments failed entirely to disclose tin placers (and associated base-metal lode deposits), whereas panned concentrates, irrespective of the concentration ratio achieved by panning, were infallible in tracking down the source area for the tin in placers.

Where tin deposits of the sulfide-cassiterite type occur, stream sediments are useful indicators of such ore deposits. In the surface environment, stannite breaks down to varlamoffite, an earthy friable tin mineral which is easily incorporated into fine-grained sediments. Because many other ore elements are found in sulfide-cassiterite deposits, tin may be accompanied in stream sediments by such elements as copper, lead, zinc, silver, tungsten, beryllium, bismuth, arsenic, and antimony, even in the clay-size or —80 mesh fraction. Typical values obtained in —40 mesh stream sediments downstream from a sulfide-cassiterite lode in northwestern Alaska are,

in parts per million: Be=41, Sn=1,100, W=70, Cu=150, Pb=150, Zn=300, As=3,000, Li=3,000. Soils developed over weakly mineralized limestones near the ore bodies gave maximum values, in parts per million, of Be=270, Cu=610, Pb=2,100, Zn=5,000, and Sn=1,500, representing enrichment factors respectively for the above elements of >180, 76, >210, >50, and 500 as compared to nearby soils over unmineralized bedrock (Sainsbury and others, 1968). Because many base-metal sulfide deposits contain some tin in sulfide minerals such as chalcopyrite, or discrete tin-sulfide minerals, tin values in the range 10–40 ppm may be found in stream sediments nearby, but they do not indicate tin lodes. In assessing small tin anomalies, it is valuable to consider the associated elements lithium, boron, and bismuth, which generally are associated with tin deposits.

For a more complete discussion of pitfalls to avoid in prospecting for tin lodes, see Hosking (1965), as well as the numerous papers presented at the First and Second International Technical Conferences on Tin (Internat. Tin Council, 1968, 1969). These volumes give excellent data on searching for both lode and placer tin deposits in various parts of the world.

Most sulfide-cassiterite tin deposits, except possibly those in Bolivia, are associated with large amounts of minerals containing fluorine and boron, especially fluorite and tourmaline. Therefore, all granites of potentially stanniferous areas which are fluoritized or tourmalinized should be carefully investigated. In fact, the worldwide association of cassiterite with fluorine or boron is sufficiently close that most workers are agreed that tin leaves the parent magma as tin complexes of fluorine and boron. It is immaterial whether we know exactly how these complexes form, or how they leave the magma; the association of tin and fluorine or boron still is a useful prospecting tool.

PROBLEMS FOR RESEARCH

The geology of lode tin deposits is well understood; the genesis of tin deposits and tin-granite remains a fertile field of debate, speculation, and little fact. Much of the recent information on the origin of tin-granites is of questionable value because of sampling and analytical difficulties, and the senior author questions whether fundamental laws will ever be shown to exist to explain the so-called tin-granites. With respect to the actual search for tin deposits, the efforts required to collect large suites of rocks, treat them in the laboratory, analyze them, and manipulate the results by complex mathematical mechanisms might well be less effective in finding ore than a similar amount of time, money, and effort invested in actual prospecting of known stanniferous areas. But no doubt geologists and geochemists will continue such investigations.

With respect to scientific studies, several areas of total ignorance are at once apparent. For instance, no information is available on the isotopic composition of tin in tin deposits. Such data are needed, though they may never lead to discovery of an ore body. Laboratory experiments are needed to duplicate the transfer of the numerous elements found together in tin deposits. Because the deposits in rhyolite are clearly formed during the crystallization of the magma, studies of fluid inclusions in these deposits would be invaluable.

The authors are unaware of any studies currently in progress that would apply isotopic studies of oxygen and sulfur to the problem of genesis of different types of tin deposits. The very exhaustive and important study of the Bolivian tin deposits by Kelly and Turneaure (1970) suggests that of all the numerous tools available to study the temperature of formation of tin deposits, as well as the composition of the ore-forming fluids, fluid-inclusion studies are by far the most usable. Their study should provide a model for much more work like theirs—detailed, factual, and with arguments based upon the observed facts. That the ore-forming solutions were high-temperature (to 560°C) highly saline solutions that probably boiled at times will not but please hydrothermalists. And the added conclusions of Kelly and Turneaure that

"The Bolivian province has provided an ideal testing ground for numerous laboratory geothermometers that have been proposed in recent years. The results obtained with the various sulfide thermometers have been generally disappointing and hardly justify the time invested."

will certainly disturb the "laboratory economic geologist" and delight the field economic geologist. If their conclusion is true, cannot one validly ask "If such rigidly controlled laboratory experiments cannot provide dependable data on even the temperature of deposition of tin deposits, how shall we ever discover (and prove) the method of generation of a tin-rich magma?"

One last and troubling problem in petrogenesis needs mention. The alkalic rocks in many parts of the world contain tin in amounts equal to or greater than the so-called tin-granites, yet no commercial tin lodes are ever associated with them. In a way, this fact refutes the possibility that the tin granites derive their tin from the surrounding rocks invaded

by the magma or that tin deposits are formed by circulating meteoric waters which set up a circulation cell about the intrusive, leaching metals from the surrounding rocks, transferring them in or alongside the intrusive and then redepositing them as the economic tin deposits. If such a mode of origin for tin deposits is to be seriously entertained, first must come a valid answer as to why tin-rich syenites, or other alkalic rocks which often rise through continental crust similar to the tin granites, do not have associated tin deposits. Research on this problem is much needed.

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TITANIUM

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ABSTRACT OF CONCLUSIONS

Titanium is an abundant element that is principally useful in the modern industrial technology of affluent societies. Titanium metal and alloys are used in the aerospace and chemical industries, and titanium dioxide is used in the welding-rod and pigment industries. Rutile (TiO_2), ilmenite ($FeTiO_3$), and titanium slag made from ilmenite are the principal raw materials from which purified titanium products are extracted. The Kroll method, involving reduction of titanium tetrachloride in an inert atmosphere, is used to obtain metallic titanium.

The United States is dependent almost entirely upon foreign sources, mostly Australia, for rutile, but has substantial reserves and production of ilmenite. In 1970, U.S. demand for titanium was 490,000 short tons, and annual demand is expected to exceed 1 million short tons by the year 2000. U.S. and world identified resources are estimated to be about 298 million and 2,000 million short tons of TiO_2, respectively. Reserves of titanium in the United States in 1970 were estimated to be about 25 million short tons of TiO_2, mostly in ilmenite.

Rutile, ilmenite, and other titanium-rich minerals occur in primary deposits in igneous and metamorphic rocks and in secondary-type sedimentary deposits, especially placer sands. Research is needed to find new domestic titanium deposits and processes for extracting titanium and other valuable coproducts from complex ores. Environmental problems may limit the mining of some titanium deposits.

INTRODUCTION

Titanium is an abundant element that has become significantly useful industrially to man only within the past 100 years. Its principal uses are related to requirements and wants of modern industrial technology and affluent societies.

Titanium is a silver-gray metal that crystallizes in the hexagonal system below 882°C and in the cubic system above 882°C; it has a density of 4.5, which is only 75 percent of the density of steel (Barksdale, 1966). At low temperatures titanium and its alloys compare favorably in strength with some steels. At higher temperatures to 800°C, the strength-weight ratio of titanium is more favorable,

but above 800°C it weakens considerably, and above 1,300°C it absorbs gases from the atmosphere and becomes brittle. This latter characteristic makes it necessary to utilize inert atmospheres or a vacuum in high-temperature processing or fabrication operations. Titanium metal has better corrosion resistance than stainless steel to sea water and other systems in which chloride ions are present. It is heavier than aluminum alloys but is much stronger and more chemically inert than aluminum.

Titanium metal is widely used in the aerospace industries and in the chemical industry (Miller, 1957; Stamper, 1970). In aircraft and spacecraft structural components, where strength to weight ratios are of great importance, the use of titanium alloys has grown rapidly. In the aircraft engine industry titanium alloys are used for parts requiring strength at high temperatures. In the chemical industry, where protection against corrosion is necessary, tubing, valves, pumps, and other plant components made of titanium alloys are widely used.

Titanium dioxides have properties of whiteness, opacity, and chemical inertness that make them especially suitable for use as pigments in paints and other surface coatings and in plastics (Miller, 1957; Stamper, 1970). Titanium dioxides have another important use, as welding-rod coatings, where they protect the surfaces of the weld from unwanted reaction with the atmosphere during welding. Other uses of titanium dioxides are in the manufacture of mineral fibers, in ceramic components for electronic equipment, in alloys, and in carbides.

Because the uses of titanium have evolved so recently, titanium and titaniferous materials are substitutes replacing other more commonly utilized materials. The production of titanium metal and titanium compounds of high purity involves complex and costly industrial processes, so these materials now are utilized as substitutes in the few applications where advantages are gained in performance or cost.

Unprocessed titaniferous magnetite ores are used in minor amounts as heavy aggregates because of their density.

The principal raw materials for the production of titanium metal and titanium products are (1) titanium ores, containing the minerals ilmenite ($FeTiO_3$), its alteration product leucoxene, and rutile (TiO_2); and (2) titanium slag made by smelting ilmenite ores (Lawthers, 1957). Ilmenite and associated leucoxene are more abundant than rutile and are produced in many countries, including the United States (Lawthers and Mark, 1957; Lynd, 1960). Rutile, however, is available in the United States only in deposits that are economically marginal or submarginal, and the United States, at present, is almost wholly dependent upon foreign sources for this material.

Two principal processes employed in converting titanium raw materials to purified usable titanium products are the chloride and sulfate processes (Barksdale, 1966). Rutile is the raw material that is preferred for the chloride process, which involves the production of titanium tetrachloride, a highly reactive liquid that must be handled under inert conditions. The titanium tetrachloride is converted to titanium dioxide of the rutile type or to titanium metal. Ilmenite, leucoxene (ilmenite with a high titanium content), and titanium slag can also be used in the chloride process.

In the sulfate process, either ilmenite (Temple, 1966) or titanium slag is treated with sulfuric acid to yield solutions from which iron sulfates produced from iron in the ore are precipitated, and the titanium remaining in the solution is then extracted by precipitation. The titanium may be in two different forms of titanium dioxide, anatase or rutile, both suitable for use as pigments.

Titanium metal is prepared commercially by the Kroll method (Stamper, 1970), which involves the reduction of titanium tetrachloride by metallic magnesium in an inert atmosphere and the formation of titanium sponge metal. Titanium sponge metal is melted in a vacuum to prevent reaction with gases in the atmosphere and is processed into titanium ingots.

The United States, as a leading industrial nation, is a major producer and consumer of titanium metal and welding rods; and as an affluent society it produces and utilizes great quantities of pigments, as reported in U.S. Bureau of Mines "Minerals Yearbooks, 1950–70." It is one of the major consumers of titanium raw materials as well as one of the major producers of ilmenite. World and U.S. production of ilmenite concentrates and Canadian production of titanium slag in the last two decades are shown in figure 72.

Production of rutile in recent years has been limited to only a few countries. Information available for rutile production in the world in recent years, as reported in U.S. Bureau of Mines "Minerals Yearbook, 1970" and "Commodity Data Summaries, 1972," is shown in table 136.

Closure of a mine in Sierra Leone in 1971 reduced world production of rutile by nearly 10 percent, leaving Australia as the only major rutile-producing country.

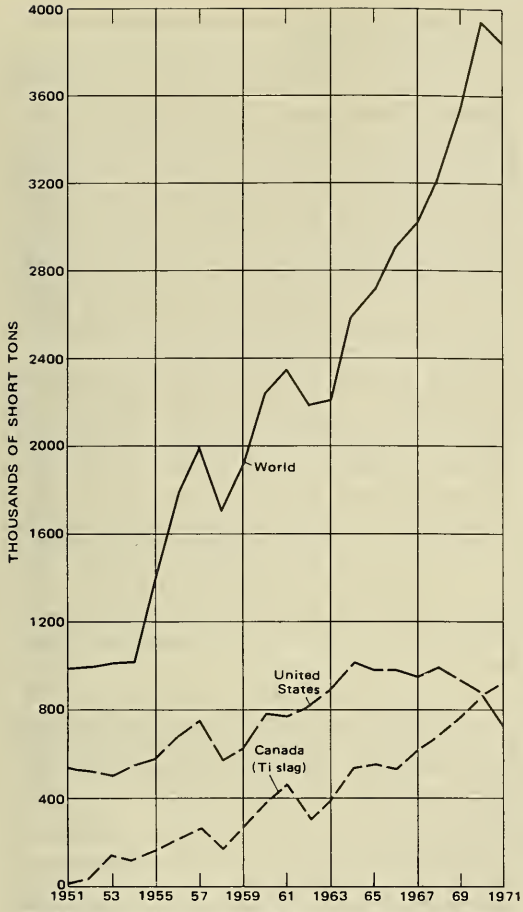

FIGURE 72.—Ilmenite concentrate production for the world and the United States, and titanium slag production for Canada, 1951–71. Data from U.S. Bureau of Mines "Minerals Yearbooks, 1950–70," and "Commodity Data Summaries, 1972."

TABLE 136.—*World production, in short tons, of rutile, 1969–71*

Country	1969	1970	1971 (estimated)
Australia	399,100	405,735	410,000
Sierra Leone	31,379	48,593	12,000
India	2,751	2,756	
Ceylon	3,036	3,000	
South Africa	543	------	
Brazil	10	Not available	
Undistributed			8,000
Total	436,819	460,084	430,000

The consumption of titanium concentrates in the United States exceeds domestic production. In 1970, the United States consumed titanium concentrates as shown in table 137 (U.S. Bur. Mines, 1972).

TABLE 137.—*U.S. consumption, in short tons, of titanium concentrates, 1970*

	Gross weight	TiO_2 content (estimated)
Ilmenite	968,926	517,256
Titanium slag	129,247	91,639
Rutile	188,290	180,642
Total estimated TiO_2		789,537

In terms of the element titanium, consumption in the United States in 1970 was about 491,000 short tons. Of this, approximately 325,000 tons was from ilmenite, 106,800 tons from rutile, and 58,800 tons from titanium slag, and the remainder from imported titanium sponge, waste, and scrap, as reported in U.S. Bureau of Mines "Minerals Yearbook, 1970."

The specific amounts of titanium used for production of various titanium products are not disclosed in order to protect data that are company confidential. However, the production capacity of the three companies that make titanium sponge metal in the United States is about 25,000 tons per year, and about 24,300 tons of titanium ingot, including alloys, was produced in 1970. Nearly 95 percent of the titanium metal consumed in the United States is used in the aircraft and spacecraft industry. Most of the remaining 5 percent is used in chemical industries and in steel making. Titanium pigment production, in terms of contained TiO_2, in 1970 was about 650,000 short tons, and more than 15,000 tons of TiO_2 was used in the production of 212,000 tons of welding rods, as reported in U.S. Bureau of Mines "Minerals Yearbook, 1970."

Although the greater part of the titanium consumed in the United States is in the form of pigment, the uses of titanium metal and titanium dioxide in the form of rutile are considered to be of strategic importance, and the Government maintains stockpiles of these materials. In December 1969, the Office of Emergency Preparedness established stockpile objectives of 100,000 short tons of rutile and 33,500 tons of titanium sponge metal. At the end of May 1972, stockpile deficits for rutile were 43,475 tons and for titanium sponge metal, 6,999 tons (Kirkemo, Harold, oral commun., 1972). Financial assistance for exploration for rutile, available from the U.S. Geological Survey, Office of Mineral Exploration, was set at 75-percent Government participation in 1967 (Stamper, 1970).

U.S. consumption of titanium raw materials greatly exceeds domestic production. The deficit is made up by imports, largely from Australia. U.S. imports of titanium concentrates in recent years are listed in table 138.

TABLE 138.—*U.S. Imports, in short tons, of the titanium concentrates, ilmenite and rutile, 1967–71*

[NA, not available; e, estimate. Data from U.S. Bur. Mines "Minerals Yearbooks, 1967–70" and "Commodity Data Summaries, 1972"]

Source	1967	1968	1969	1970	1971
Ilmenite					
Australia	60,689	45,196	28,524	96,123	NA
Canada (Ti slag)	147,216	132,958	82,329	134,996	NA
Other countries	1	----	----	----	NA
Total	207,906	178,164	110,853	231,119	150,000e
Rutile					
Australia	153,768	171,847	176,550	223,407	200,000+e
Sierra Leone	13,129	1,348	26,442	19,682	NA
Canada	----	1,171	262	180	NA
Other countries	203	----	1,673	----	NA
Total	167,100	174,366	204,927	243,269	200,000+e

The United States has large reserves of ilmenite and modest potential resources of rutile. However, competition from foreign sources, the relatively low grade of some domestic deposits, the relatively high cost of production from such deposits, and other factors have prevented the development of production capability to satisfy domestic needs. Specifically, the availability of rutile from foreign sources has, to some extent, delayed the development of additional facilities for production of synthetic rutile from ilmenite-derived titanium dioxides utilizing domestic ores.

EXPLOITATION

Within the last two decades, 1951–70, there has been more than a four-fold increase in world production of primary titanium—from less than 400,000 short tons in 1950 to 1.78 million tons in 1970 (U.S. Bur. Mines, 1972). During this period, demand for primary titanium in the United States more than doubled, reaching about 490,000 short tons in 1970. Titanium scrap consumption in 1969 was 22,800 tons (Gray and McIlroy, 1971). Demand for titanium in the United States is expected to be between 1.1 million short tons and 2.6 million short tons by the year 2000.

The greater demand for titanium has increased demand for rutile, which is the preferred raw material for production of titanium metal or pigments. Because rutile supplies in deposits of economic grade are limited and production has risen, greater reserves are needed to meet future demand. Interest has increased in developing improved processes for upgrading ilmenite and for processing it to produce titanium products.

The mining of rutile and ilmenite from placer sand deposits involves the excavation and handling of unconsolidated material, and relatively low grade placers can be worked profitably. Monazite-zircon-ilmenite deposits containing as little as 3–4 percent heavy minerals have been worked; these contained 0.5–1.5 percent TiO_2. Other deposits having various mixtures of the minerals monazite, zircon, ilmenite, leucoxene, rutile, garnet, and staurolite are worked in Florida and New Jersey. The heavy minerals are concentrated and then separated by use of Humphrey spirals and electromagnetic and electrostatic separators (Quirk and Eilertsen, 1963).

Mining of primary ilmenite deposits such as those at Tahawus, N. Y., involves drilling, blasting, and crushing of hard-rock ore, followed by fine grinding, magnetic separation, and hydraulic classification. The cost of these operations is high, but the crude ore contains about 16 percent TiO_2, which is upgraded to concentrates containing 45 percent TiO_2. In addition to the titanium concentrate, magnetite ore containing 56 percent iron is recovered. The ilmenite ores also contain 0.24 percent vanadium pentoxide (V_2O_5), which is a potentially recoverable valuable constituent. (See chapter on "Vanadium.")

PRICES, VALUE OF IMPORTS

The prices of some titanium raw materials and of some titanium products are indicated in the following list taken from data compiled from published sources for 1970 (Noe, 1972).

Specification of material	*Price*
Ilmenite, domestic (60 percent TiO_2), per short ton	$30.00– $35.00
Ilmenite, imported (54 percent TiO_2), per long ton	20.00– 21.00
Rutile, imported (96 percent TiO_2), per long ton	160.00– 185.00
Titanium slag, imported (about 70 percent TiO_2), per long ton	45.00
Rutile grade titanium dioxide, per pound	.26– .27
Titanium sponge, domestic, per pound	1.32
Titanium sponge, imported (from Japan and Britain), per pound	1.20– 1.25

The value of imported rutile in 1970 was $19.8 million, and the combined value of imported ilmenite and titanium slag was $6.4 million. Unwrought titanium metal waste and scrap valued at $10.5 million were also imported in 1970.

BYPRODUCTS AND COPRODUCTS

Titanium deposits in various parts of the world commonly are worked for more than one product.

In some places, titanium minerals are merely byproducts, and the exploitation of the deposits is dependent upon market conditions for the other minerals.

The major byproducts and coproducts recovered from titaniferous ores are iron-ore concentrates, monazite, and zircon. Vanadium is obtained from some titaniferous ores and is potentially recoverable from many primary ilmenite deposits (Jones, 1965). Potential coproducts from secondary deposits resulting from lateritic weathering of the primary minerals are iron ores, aluminum ores, and nickel, cobalt, and chromium concentrates.

In deposits of rutile such as those near Evergreen, Colo., topaz is a possible coproduct.

Rutile has been recovered from deposits worked for gold, diamonds, platinum, and tin. Other heavy minerals which contain columbium, tantalum, uranium, and rare earths are potential byproducts of titanium.

It is likely that future titanium mining and processing will involve increased recovery of coproduct and byproduct materials.

ENVIRONMENTAL PROBLEMS

Environmental problems related to titanium production are physical hazards, land despoilment, and pollution, which are the same as those related to other types of metal mining, processing, and fabrication. Mining of primary deposits produces open-cut pits and underground workings in which falling rock, landslides, or land subsidence present direct physical dangers. These dangers, however, can be minimized by taking ordinary but at times costly precautions. Land despoilment in the mining of secondary deposits in particular can be a major problem. Large areas along beaches and in terrace deposits away from shorelines may be excavated. These can be reclaimed by releveling in many places, if the deposits are sufficiently valuable that the costs of reclaiming the land can be covered by the profits derived from mining. Some lands, however, have high surface values, particularly in inhabited and recreational areas, and deposits in such places may not be minable. Pollution by particulate matter, such as sand and silt in streams and along some shores, may be difficult or impossible to control if some deposits are mined. Another major problem is the disposal of large quantities of sulfates and other chemicals that accumulate in waste products that result from the chemical processing of titanium ores.

In present and future mining and processing of titanium ores, the environmental problems require a great deal of consideration if the operations are to be conducted profitably. In many places, deposits may not be mined or mining may be curtailed because of conflicting environmental considerations.

GEOLOGIC ENVIRONMENT

GEOCHEMISTRY

Titanium is the ninth most abundant element, following oxygen, silicon, aluminum, iron, calcium, magnesium, sodium, and potassium, which make up more than 98 percent of the earth's crust. The remaining 84 elements are commonly considered to be trace elements.

Titanium is a lithophile element and has a strong affinity for oxygen. It is in group IVA of the periodic table, along with zirconium and hafnium. Titanium, zirconium, and hafnium have approximately the same abundance ratio (Ti:Zr:Hf= 1,000:50:1) in igneous rocks, in silicate meteorites, and in the solar atmosphere (Rankama and Sahama, 1950).

Because titanium is strongly lithophilic, it concentrates in stony matter of the "slag crust" of the earth as well as in the stony matter of meteorites (Goldschmidt, 1954, p. 409). Oceanic crust and continental crust contain about 8,100 ppm (parts per million) and 5,300 ppm titanium, respectively (Lee and Yao, 1970). It forms oxides and oxy-salts and has no tendency to concentrate in metallic iron or to form sulfides. Titanium tends to be incorporated in ilmenite ($FeTiO_3$) and sphene ($CaTiSiO_5$). The greatest abundance of titanium is in subsilicic rocks, including mafic and alkalic rocks, or is associated with anorthosites. The abundance of titanium in different rock types in percent is (Vinogradov, 1962): stony meteorites, 0.05; ultramafic rocks, 0.03; mafic rocks, 0.9; intermediate rocks, 0.8; felsic rocks, 0.23; and sediments, 0.45.

The behavior of titanium in magmatic crystallization is complicated and depends on such factors as the initial titanium content of the magma, the chemical activities of iron, silicon, and aluminum, the partial pressure of oxygen, and the temperature of crystallization. Thus, in some magmas titanium will enter silicate minerals at high temperatures rather than form oxides (Verhoogen, 1962).

Titanium commonly occurs in clinopyroxenes, olivine, biotite, amphibole, and sphene. In crystallizing magmas, Ti-Fe oxides will form in two ways: (1) by direct precipitation of ilmenite or ilmenite-hematite solid solution or ulvospinel-magnetite solid solution; the earliest formed oxides will have the highest Ti/Fe ratios; (2) by breakdown of

iron-bearing pyroxenes at low oxygen pressures to form ilmenite and iron-free pyroxene.

Because of its strong affinity for oxygen, most of the titanium in the lithosphere is in oxide minerals. The three common titanium minerals are ilmenite, rutile, and sphene; of these, ilmenite is by far the most common, accounting for more than 90 percent of the titaniferous constituents of igneous rocks. In some igneous rocks where rapid crystallization has occurred, the titanium has combined with magnetite to form titanium-magnetite; titanium is also present in minor amounts in many other minerals.

TITANIUM-RICH MINERALS

Rutile is one of three titanium dioxide minerals but has somewhat different physical characteristics from anatase (octahedrite) and brookite, the other two dioxides. Some physical characteristics of these and other titanium-rich minerals are listed in table 139. The percentage of titanium dioxide in these minerals is a measure of the percentage of titanium dioxide that can be obtained in concentrates of each of these minerals. Their high specific gravities indicate that they can be separated from more common light minerals by gravity methods. The indices of refraction of the three varieties of titanium dioxide minerals are a measure of the opacity of these crystalline forms. This is of importance in their use as pigments, as "covering power" of the pigment is related to the opacity of its constituents. White pigments of high opacity and high degree of chemical inertness can be made from rutile and anatase.

The principal titanium minerals form primarily as products of the crystallization of igneous magmas and as recrystallization products in metamorphic rocks. Rutile deposits occur as local concentrations in igneous and metamorphic rocks, in veins associated with igneous and metamorphic rocks, and as concentrations in sedimentary rocks and unconsolidated sediments derived from the weathering of rutile-bearing rocks.

PRIMARY RUTILE DEPOSITS

Rutile occurs primarily in alkalic igneous rocks, in alkalic noritic-anorthositic complexes, and in granitic and syenitic veins and pegmatites. It is also formed in aluminum-rich high-grade metamorphic rocks and in high- and low-grade metamorphosed mafic and ultramafic rocks. All economic primary rutile deposits are in the noritic-anorthositic complexes. Few primary rutile deposits are of economic value, however, and most primary rutile is recovered as a product of ilmenite mining.

At Kragero, Norway, rutile occurs in an aplite dike associated with gabbro that contains an average of 5–10 percent rutile. In the United States, in Amherst and Nelson Counties, Va. (Hillhouse, 1960; Ross, 1941), rutile occurs as an abundant mineral in dikelike or lenticular bodies of nelsonite, an ilmenite-apatite-rutile-rich rock, associated with a larger body of anorthosite. Some of the nelsonite contains as much as 60 percent rutile. Rutile also occurs in the anorthosite as disseminated grains averaging 4–5 percent of the rock and in quartz-rutile stringers containing as much as 30 percent rutile. Rutile has been mined from nelsonite dikes adjacent to, and disseminations in, anorthosite at Roseland, Va. (Peterson, 1966). It has also been produced from an alkalic igneous complex at Magnet Cove, Ark.(Fryklund and Holbrook, 1950). In the Magnet Cove area, rutile and brookite occur in association with novaculite and aegirine phonolite porphyry. The rutile in that area is in carbonate-feldspar veins that cut the porphyry, and the brookite occurs as crystals in quartzite masses embedded in the novaculite. Chloritic ultramafic rock in Harford County, Md., contains about 5 percent rutile in association with abundant magnetite, apatite, and ilmenite, on the flank of a serpentinized ultramafic body (Herz and Valentine, 1970).

In Mexico, rutile is associated with anorthosite at Pluma Hidalgo, Oaxaca (Roy, 1970a); and in Canada, rutile occurs in ilmenite-rich anorthosite in the St. Urbain area, Quebec (Rose, 1969).

Potentially economic deposits of rutile occur near Evergreen in the Front Range of Colorado as fine disseminations in fluorine-metasomatized light-

TABLE 139—*Principal titanium-rich minerals*

[Leucoxene, an alteration product of other titanium minerals, contains more than 60 percent TiO_2. Data from Deer and others (1962); Lawthers (1957)]

Mineral	Formula	TiO_2 percentage		Specific gravity	Range of indices of refraction	Crystal system
		Theoretical maximum	Minimum			
Anatase	TiO_2	100	98.2	3.90	2.488–2.561	Tetragonal.
Brookite	TiO_2	100	98.8	4.14	2.583–2.700	Orthorhombic.
Rutile	TiO_2	100	45.7	4.21	2.612–2.899	Tetragonal.
Ilmenite	$FeTiO_3$	52.7	46.2	4.72	----------	Hexagonal.
Perovskite	$CaTiO_3$	58.9	38.7	4.01	2.30–2.37	(Pseudoisometric, monoclinic?)
Sphene	$CaTiSiO_5$	40.8	33.7	3.4–3.56	1.900–2.034	Monoclinic.

colored high-grade gneiss (Sheridan and others, 1968). These deposits are thought to have been originally laterites or bauxites that contained resistant titanium minerals. The rutile forms about 2–4 percent of the gneiss.

SECONDARY RUTILE DEPOSITS

Secondary deposits of rutile derived from the weathering of primary occurrences of rutile are the most important types of rutile deposits currently mined. These consist mainly of marine placer sands, stream sands and gravels, and lag saprolite deposits. Rutile, having a specific gravity greater than 4.0, is concentrated in placers with other heavy minerals by wave and stream action, in loose sands along coastal areas and along streams. In addition to deposits along modern shores, important quantities of rutile are contained in buried placers in terraces inland from present shorelines. Such deposits commonly have other valuable heavy minerals such as ilmenite and zircon, and some heavy-mineral deposits, in which monazite is the most abundant and the most important heavy mineral, also contain significant amounts of rutile. Similar deposits probably occur in offshore areas near coasts where shoreline rutile deposits indicate availability of suitable types of sediments. Formerly commercial deposits in lag saprolite deposits derived from weathering of titanium-bearing rock are present in Amherst and Nelson Counties, Va. (Fish, 1962; Herz and others, 1970), as well as in Hanover County. The Magnet Cove, Ark., rutile deposits also include some occurrences of the saprolitic type.

PRIMARY ILMENITE DEPOSITS

Some of the more important and currently economic primary ilmenite deposits are in the U.S.S.R., the United States, Canada, and Norway (Lawthers, 1957; Peterson, 1966; Rose, 1969; Roy, 1970a). In the Ilmen Mountains (part of the Ural Mountains) of the U.S.S.R. (Lawthers, 1957), large economic deposits of ilmenite and titaniferous magnetite also contain important amounts of vanadium. The titanium-iron ores there measure in the hundreds of millions of tons. Other ilmenite deposits in the U.S.S.R. are known in the Kola Peninsula and in the Ukraine. In the United States, ilmenite-magnetite deposits in gabbro and anorthosite at Tahawus, Essex County, N. Y. (Peterson, 1966) are a major source of titanium. Economic deposits of ilmenite, hematite, and magnetite occur as segregated masses in gabbro and anorthosite in the Tellnes deposit, Norway, and high-grade ilmenite ores in amphibolite at the Otanmaki deposit in Finland (Paakkonen, 1956) are mined. Important commercial deposits of ilmenite, magnetite, and rutile in gabbro-anorthosite are worked in the St. Urbain area, Quebec, Canada. Large deposits of ilmenite and titaniferous magnetite in the Bushveld Complex of South Africa are important for their vanadium content.

SECONDARY ILMENITE DEPOSITS

Most titanium minerals are relatively resistant to weathering and are commonly found in resistate sediments. Ilmenite forms most of the economic secondary deposits of titanium; these deposits are placer sands that occur throughout the world. In general, they are in areas peripheral to regions having host rocks containing primary titanium mineral deposits. During the weathering of ilmenite, iron is released and titanium forms a simple dioxide, leucoxene, which is commonly present in placers. The placer deposits of ilmenite, rutile, and leucoxene commonly contain other heavy minerals, such as zircon and monazite, in significant amounts.

Placer deposits of ilmenite and other titanium minerals occur along present-day beaches where wave action sorts and concentrates the heavy minerals, and in deltas and along streams where heavy minerals settle from the slower moving water. Fossil placers of ilmenite in sedimentary rocks are also known where similar mechanisms in the past have concentrated the heavy minerals. Some placer deposits have been derived from older detrital deposits. The coastal areas of all the inhabited continents have significant ilmenite placer deposits. Important deposits in the United States are in northern Florida and near Lakehurst, N. J.

Fossil placer deposits in the United States near Highland and Starke, Fla., are at present being mined for ilmenite, rutile, and zircon, which were originally derived from the crystalline rocks of the Piedmont area (Pirkle and Yoho, 1970). At Lakehurst, N. J., a fossil placer of ilmenite is being mined from heavy-mineral lenses in sediments of Cretaceous and Tertiary ages. Reworking has concentrated the heavy minerals into an economic deposit (Markewicz, 1969).

Australia is the leading producer of titanium minerals with a production of 0.98 million tons of ilmenite in 1970 (Lynd, 1972) from the coastal sands of Western Australia. Rutile, zircon, monazite, and ilmenite are also recovered from deposits on the coast of Queensland and New South Wales. In 1970, Australia produced 405,735 short tons of rutile, about 89 percent of world production (Lynd, 1972). New Zealand also has large resources of coastal black-sand deposits of ilmenite, which are currently

being investigated (Lynd, 1972). In Brazil, a deposit of beach sand was mined for ilmenite in southern Bahia (Roy, 1970b).

Other secondary titanium occurrences are concentrations of titanium dioxide in residual deposits formed by lateritic weathering of titaniferous rocks, many in areas having tropical climates. Titanium in the common rock-forming silicate minerals is hydrolyzed upon weathering and carried into the hydrolyzates (bauxites and other laterites) where it forms oxide minerals (Rankama and Sahama, 1950). Goldschmidt (1954) stated that the compounds in which this titanium occurs are not known but that the titanium may be present as amorphous or finely crystalline titanium dioxide. These lateritic deposits are not of commercial value at present but are widespread in Hawaii and elsewhere. A major nontropical occurrence is found in the lateritic ferruginous bauxites from the Columbia River Basalt in Oregon, which contain 3.5 million short tons of TiO_2 (Herz, 1969).

RESOURCES

IDENTIFIED TITANIUM RESOURCES

The identified titanium resources in the United States, in terms of contained TiO_2, are about 298 million short tons. The distribution of these resources by States is shown in table 140.

TABLE 140.—*Identified titanium resources, in thousands of short tons, in the United States*

[NA, not available. Data from Herz (1969); Hillhouse (1960); Peterson (1966); Stamper (1970)]

State	TiO_2
Alabama	143
Alaska	127,000
Arkansas	70
California	840
Colorado	673
Florida	20,615
Georgia	NA
Hawaii	51,434
Idaho	315
Minnesota	14,414
Montana	270
New Jersey	12,500
New Mexico	609
New York	23,960
North Carolina	71
Oklahoma	4,941
Oregon	3,500
Rhode Island	686
South Carolina	2,716
Utah	188
Virginia	12,000
Washington	890
Wyoming	20,000
Total	297,835

The data given in this tabulation are only an approximation, because the source material upon which the estimates are based is incomplete and some of the data have not been corrected for amounts depleted by mining.

In the States of Florida, Georgia, New Jersey, New York, Virginia, North Carolina, and South Carolina, where secondary or primary deposits have been mined for titanium minerals, identified resources are estimated to be about 72 million tons of contained TiO_2. Titanium reserves in the United States were estimated by the U.S. Bureau of Mines in 1970 (Stamper, 1970) to be about 25.5 million short tons of TiO_2, most of which is in ilmenite. Reserves of rutile included in this figure were reported to be 500,000 tons, but inasmuch as rutile production in the United States has virtually ceased, this rutile may be more realistically considered to be only a conditional resource.

The identified titanium resources of the world, in terms of TiO_2, are about 2,000 million short tons. Distribution of these resources is listed in table 141.

TABLE 141.—*Identified titanium resources, in thousands of short tons, of the world*

[Identified resources: Specific, identified mineral deposits that may or may not be evaluated as to extent and grade, and whose contained minerals may or may not be profitably recoverable with existing technology and economic conditions. Data from Herz (1969); Hillhouse (1960); Lawthers (1954, 1957); Peterson (1966); Stamper (1970); United Nations (1970); U.S. Bur. Mines "Mineral Trade Notes, 1950–70," "Minerals Yearbooks, 1950–70," and "Commodity Data Summaries, 1972;" Williams (1965)]

Continent and country	TiO_2
North America:	
United States	297,835
Canada	397,374
Mexico	4,812
Costa Rica	1,390
Total	701,411
South America:	
Argentina	3,114
Brazil	4,525
Guyana	18,548
Uruguay	912
Total	27,099
Australia and New Zealand:	
Australia	15,068
New Zealand	42,130
Total	57,198
Europe:	
Finland	6,750
France	3,208
Norway	43,836
Sweden	24,728
U.S.S.R.	73,404
Total	151,926
Africa:	
Angola	331
Dahomey	15
Madagascar (Malagasy Republic)	1,045
Mauretania	144
Mozambique	5,884
Senegal	3,440
Sierra Leone	2,490

TABLE 141.—*Identified titanium resources, in thousands of short tons, of the world*—Continued

Continent and country	TiO_2
Africa—Continued:	
South African Republic	761,384
South West Africa	5
Spanish Sahara	8,819
Tanzania	6,449
Uganda	5,156
United Arab Republic	16,660
Upper Volta	6,614
Total	818,436
Asia:	
Burma	678
Ceylon	2,849
China, People's Republic	744
Taiwan	27
India	196,726
Indonesia	1,819
Japan	9,052
Korea	826
Malaysia	82
North Vietnam	4
Pakistan	849
Philippines	807
Saudi Arabia	69
Thailand	8
Total	214,540
World total	1,970,610

The amounts listed are considered to be very conservative, because quantitative estimates of the potential titanium resources in many of the large complexes of mafic rock in various parts of the world are not included.

Because rutile is the preferred raw material for the chemical extraction of titanium in commercial practice, the resources of rutile are worthy of consideration separately, even though they are included in the titanium resources listed in table 141. Identified resources of rutile in some principal primary and secondary deposits are listed in table 142.

Although the identified titanium resources of the world are large, less than 10 percent of these resources can be considered as titanium reserves. Recent estimates made by the U.S. Bureau of Mines (Stamper, 1970) of world reserves of titanium show nearly 147 million short tons of contained titanium, which is equivalent to about 247 million tons of TiO_2. The distribution of these reserves is shown in table 143. As for total identified resources, the reserve data are considered to be very incomplete.

HYPOTHETICAL RESOURCES

Hypothetical resources of titanium are large, but difficult to quantify. Because the estimates of identified resources for the world include more than 90 percent potential ores in known districts and less than 10 percent reserves, those estimates, to some degree, may include some hypothetical ores. Some coastal areas, into which extensions of deposits of titaniferous sands can be projected, are excluded

TABLE 142.—*Identified world resources, in thousands of short tons, of rutile*

[Identified resources: Specific, identified mineral deposits that may or may not be evaluated as to extent and grade, and whose contained minerals may or may not be profitably recoverable with existing technology and economic conditions. Data from Barksdale (1966); Hillhouse (1960); Lawthers (1954, 1957); Lynd (1972); Peterson (1966); Rose (1969); Stamper (1970); U.S. Bur. Mines "Mineral Trade Notes, 1950–70" and "Minerals Yearbooks, 1950–70"]

Country	Rutile
Canada:	
St. Urbain	300
United States:	
Amherst and Nelson Counties, Va.	450– 1,150
Magnet Cove, Ark.	500
South Carolina monazite belt	1,100
Florida and Georgia deposits	650
Mexico:	
Pluma Hidalgo, Oaxaca	5,000–25,000
Brazil:	
Paranaíba delta, State of Maranhão	500
State of Sergipe	300
Uruguay:	
Aguas Dulces	27.2
Argentina:	
Buenos Aires Province	1.9
Sierra Leone:	
Bonthe (Sherbro) area	1,500–30,000
Cameroons:	
Yaounde River	[1]
Senegal:	
Coast north of Dakar	100
South Africa:	
Orange Free State	500
Natal	170
South West Africa:	
Area north of Karibib	5
U.S.S.R.:	
Ukraine	[2] 300
India:	
Kerala State	100
Ceylon:	
Pulmoddai and Kokkilai area	300
Australia:	
Eneabba, west coast of Western Australia	[3] 1,000
Coast of Queensland	6,900
Coast of New South Wales	

[1] Past production data available, but no reserve data.
[2] Data incomplete.
[3] Undeveloped.

TABLE 143.—*World reserves, in thousands of short tons, of titanium*

[Reserves: Identified deposits from which minerals can be extracted profitably with existing technology and under present economic conditions. Data from Stamper (1970)]

Country	Ilmenite	Titanium equivalent	Rutile	Titanium equivalent
United States	100,000	25,000	500	250
Australia	20,000	5,000	4,000	2,000
Canada	100,000	25,000	300	250
Ceylon	5,000	1,250	500	150
India	60,000	15,000	100	50
Norway	120,000	30,000		
Sierra Leone	-----	-----	3,000	1,500
U.S.S.R.	100,000	25,000	300	150
United Arab Republic	40,000	10,000	----	----
Others [1]	25,000	6,250	----	----
Total	570,000	142,500	8,700	4,350

[1] Comprise Finland, mainland China, Malaysia, Japan, Spain, and Brazil.

from consideration because of the probable environmental damage to scenic and recreational areas that would result from mining. In sparsely inhabited areas, especially in developing nations, such considerations may not be deterrents to mining. Political considerations in the developing nations may temporarily have a great influence on mining activity.

Placer deposits in some coastal areas are partially renewable over periods of years or decades because of continuous reworking of the sands by waves and currents. The grade of the deposits decreases as the sands are mined repeatedly.

Deposits such as the titaniferous magnetite bodies and the titaniferous gabbros in the State of New York are irregular in form, and their projection to greater depths or in lateral directions can be done with reasonable certainty only for individual deposits. They can, however, be considered collectively as being representative of the concentrations of titanium in their host rocks to a specified depth. Inasmuch as the concentrations of titanium in deposits of this type are not related to enrichment relative to the present surface, the quantity of titanium in such concentrations for each additional increment of depth should tend to average near the amount that exists in the shallow zone. For example, if nearly 24 million short tons of TiO_2 has been identified in the uppermost 500 feet of the districts that have been explored in New York, it is likely that an equivalent amount will exist between depths of 500 and 1,000 feet in these districts.

Hypothetical resources of titanium in the United States are estimated to be about 155 million short tons TiO_2. This quantity represents only a 53-percent addition to the identified titanium resources, and most of this increase is for primary-type ilmenite deposits. Among these, magnetite-ilmenite deposits of northern New York and eastern Minnesota are high-grade deposits, favorably located with respect to markets. Very large low-grade magnetite-ilmenite deposits in Alaska are distant from markets but are along the coast and are accessible. Primary ilmenite-rutile deposits in Virginia and their associated placer deposits are also favorably located geographically, but competitive land-use considerations could render the placers unavailable. Primary magnetite-ilmenite deposits in Wyoming may contain large hypothetical resources. Placer deposits in Florida, Georgia, South Carolina, North Carolina, and New Jersey contain large tonnages of hypothetical resources of titanium. Some of these are also important for monazite, zircon, and other heavy minerals.

Any attempt to assign quantitative estimates to hypothetical resources of titanium must be made with the recognition that the resource data are incomplete. Hypothetical resources based on modest projections of identified resources and on interpretations of the extent of exploration effort and production records for certain regions are shown in table 144.

TABLE 144.—*Hypothetical world resources, in millions of short tons, of titanium*

[Hypothetical resources: Undiscovered mineral deposits, whether of recoverable or subeconomic grade, that are geologically predictable as existing in known districts]

Continent	TiO_2
North America	400
South America	200
Australia and New Zealand	100
Europe	200
Africa	500
Asia	200
Total	1,600

SPECULATIVE RESOURCES

Speculative resources of titanium are very great. Ilmenite is a common mineral in mafic and ultramafic rocks such as those of the Bushveld Complex of South Africa, in anorthosites of the Canadian Shield, and in similar rocks of Precambrian shield areas of each continent. Many tens of billions of tons of such rocks containing a few percent of ilmenite are within a depth of less than 1 mile beneath the surface of the earth, and exploration of these great rock units should disclose large bodies having higher than average amounts of ilmenite.

Bauxite and other lateritic deposits containing aluminum, iron, chromium, cobalt, nickel, and a few percent TiO_2 are also potential sources of titanium. Lithified placer deposits in sedimentary rocks, such as the extensive black sand deposits in the Upper Cretaceous formations of Wyoming and also present in Arizona, New Mexico, Utah, Colorado, Idaho, and Montana (Dow and Batty, 1961; Houston and Murphy, 1962), indicate the possibility of significant resources of titanium minerals in sandstone deposits. Metamorphic equivalents of similar titanium-rich sedimentary rocks and of some mafic plutonic rocks offer additional possibilities for titanium ores. Offshore placer deposits paralleling known coastal placer deposits and placer deposits along coasts where the shallow marine sediments were derived from titaniferous rocks should contain concentrations of titanium minerals equivalent to those in shoreline placers or in terrace deposits in raised beaches (McKelvey and Wang, 1969). In many parts of the world the areas favorable for

offshore titanium placer deposits are large in comparison with the areas of shoreline placer deposits, and the potential resources therefore are large. If mining of sea-floor manganese nodules becomes a practical source of metals, as suggested by Mero (1965), another source of titanium as a byproduct would be developed. New techniques for economic development of this potential source of metals will determine the possibility of such mining becoming commercial in operation.

Quantitative estimates of the world's speculative resources of titanium, in terms of contained TiO_2, are given below: (Speculative resources are undiscovered mineral deposits, whether of recoverable or subeconomic grade, that may exist in unknown districts or in unrecognized or unconventional form.)

Type of deposit	*Size*
Primary:	
Ilmenite, magnetite, rutile, anatase, brookite, perovskite, and sphene in igneous and metamorphic rocks	Large (tens of billions of tons).
Secondary:	
Unconsolidated placers. Consolidated placers in fairly unmetamorphosed sedimentary rocks	Intermediate (billions of tons).
Residual:	
Lateritic and saprolitic concentrations in surficial zones	Small (hundreds of millions of tons).
Sea-floor nodules:	
Iron- and manganese-rich nodules containing minor amounts of titanium	Small.

EXPLORATION

Exploration for titanium deposits has been directed largely toward the discovery of well-known types of primary deposits, such as the occurrences of ilmenite and titaniferous magnetite in association with mafic and ultramafic rocks, or toward the discovery of secondary deposits of titaniferous heavy minerals in placers. Background geologic information concerning the occurrence of favorable host rocks or known mineral occurrences is used to provide a basis for selecting target areas for exploration. Because most primary ilmenite deposits contain large amounts of magnetite, these deposits have associated magnetic anomalies. Such anomalies are detected by aeromagnetic surveying, and after anomalous areas are located, they are studied in more detail by ground magnetic surveys, gravity surveys, and detailed geologic mapping. Titaniferous magnetite deposits commonly have somewhat more complex magnetic anomalies than those associated with most nontitaniferous magnetitic iron deposits and thus require sophisticated geophysical interpretations. High-grade ilmenite deposits have higher densities than their host rocks and are therefore detectable by the gravity anomalies that reflect the differences in density between the ore deposits and their host rocks. Combined magnetic and gravity data interpreted in conjunction with other geologic data are used to pinpoint target areas for drilling and sampling. The sampling and the analyses of the samples provide the basis for evaluation of deposits that are discovered.

In exploration for placer deposits, coastal areas, known areas of fossil placers, and terrace deposits along streams are sampled, and heavy-mineral concentrates from the samples are analyzed to determine their mineral and chemical compositions. Wherever possible, interpretations are made of sedimentary features, such as ancient stream channels, beaches, offshore bars, and sand dunes. Other sedimentary parameters used are grain size and composition; these make it possible to reconstruct the probable conditions of deposition and concentration of heavy minerals and to determine the probable extent of favorable concentrations of the minerals sought.

Many placer concentrations of heavy minerals contain radioactive minerals. Such deposits can be detected by aerial or ground radiometric surveys, provided that the deposits are not covered by too great a thickness of overburden. Aerial albedo surveys will probably be used more in the United States as quantitative albedo measurements become feasible.

Once the favorable target areas are located, they must be tested by sampling in order to determine the economic potential of the deposits. The samples must be analyzed, and factors such as the quantity and quality of the recoverable ore and the ratio of overburden to ore must be determined.

PROBLEMS FOR RESEARCH

The cost of processing the abundant titanium mineral, ilmenite, to obtain usable titanium dioxide or titanium metal is so much higher than that of processing natural rutile that despite its relative scarcity and higher cost in world markets, rutile is preferred as a source of titanium. So long as rutile is obtainable from foreign sources at lower cost than that produced in the United States, domestic rutile deposits of lower grade and higher production cost are noncompetitive. Geologic exploration is needed to find large and higher grade domestic rutile de-

posits. Such exploration can be guided by known geologic data or by development of new geologic and mineralogic concepts that will make it possible to discover previously unrecognized types of deposits. Extensive sampling and analyses of many rock types are needed to obtain additional background data on the occurrence and distribution of titanium, not only in ilmenite and rutile but also in sphene, perovskite, and other titanium minerals.

Geologic search for titanium resources might be based upon a reexamination of analytical and geologic data that are already available for many large rock units and upon reinterpretation of possible geologic environments in which titanium may be concentrated. For example, search could be made for sedimentary deposits containing titanium minerals that had been primary segregates in the eroded upper parts of the Stillwater Complex in Montana or of other major gabbroic and anorthositic rock units, such as the Duluth Gabbro in Minnesota. Such studies of sedimentary rocks in the U.S.S.R. have related heavy-mineral concentrations in rock formations of various ages to the source rocks and to erosional and depositional histories of the sediments (Gurvich and others, 1965). Greater use might be made of data available from drilling for oil and gas, not only for knowledge of depositional environments of titanium but also for information concerning the mineralogical composition of sedimentary rocks.

The portion of the titanium industry that is equipped to use ilmenite or other minerals rather than rutile can be expected to increase in view of the abundance of ilmenite and the relative scarcity of rutile. This change is likely to be slow, but, as in the case of the iron-ore industry turning to taconite ores, in the long run the titanium mineral processing industry may find it profitable to place greater emphasis on the use of the abundant titanium raw material ilmenite.

The current small market for titanium is a limiting factor in the development of large low-grade deposits of ilmenite and of improved methods for extracting the titanium from such ores. This is also true for possible multiproduct ores such as laterites. The separation of the major mineral industries into those producing iron, aluminum, titanium, and other metals has not favored the development of mineral beneficiation of complex multiproduct ores, but such development is needed. A specific example in which this development could affect the titanium industry is the future utilization of the titanium and many other components of sea-floor manganese nodules (McKelvey and Wang, 1969; Mero, 1965). The technology needed for recovery of sea-floor nodules involves a large increase in scale of dredging over that currently done for finer grained materials in shallow waters. Separation of the metallic components of the nodules into usable and marketable products is a chemical or metallurgical problem.

Both chemical and metallurgical research are needed to improve methods of processing mineral raw materials in general, because such improvements result in great additions to the quantities of useful mineral resources. The excess of titaniferous magnetite concentrates obtained from primary ilmenite ores might be converted to usable iron ore, and an increase in recovery of ilmenite might be achieved by improved mineral beneficiation methods.

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TUNGSTEN

By S. Warren Hobbs and James E. Elliott

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ABSTRACT OF CONCLUSIONS

Most of the major tungsten deposits of the world have a close spatial and genetic association with granitic intrusive rocks or their related porphyries. Although several very diverse modes of occurrence are recognized, more than 95 percent of all tungsten production has come from three types of deposits: contact-metamorphic deposits (tactites), quartz veins, and stockworks. A close genetic association between igneous rock and ore is strongly suggested by the localization of many ore bodies of these kinds within or adjacent to the roof zones of major intrusive bodies, or close to cupolas, stocks, and bosses.

U.S. tungsten reserves in known deposits or their geologically reasonable extensions are estimated at 15 million short ton units (1 short ton unit=20 pounds WO_3). This is about 6.8 percent of known world reserves, of which approximately 60 percent are in China. Subeconomic resources in identified or geologically plausible deposits in the United States are conservatively estimated to contain two to three times the reserves. Covered areas in the United States probably contain concealed deposits that are comparable in grade and total tonnage to those now known.

The United States has the potential for adequate tungsten production into the foreseeable future, provided it is willing to pay the price of essential research, extensive exploration, and the processing of high-cost low-grade ores.

INTRODUCTION

Tungsten in its pure form is a silver-gray or tin-white metal of high specific gravity (19.35) whose usefulness is related directly to its special or unique physical and mechanical properties: the metal has, next to carbon, the highest melting point of all the elements (3,400°C); its tensile strength (maximum of 590,000 lbs per sq in.) is the highest of all metals; and its high heat of sublimation, low compressibility, and low coefficient of thermal expansion are further attributes of importance in certain applications. These fundamental properties are due to the nature of the crystalline lattice of tungsten atoms. Tungsten is one of the so-called transition metals which are characterized by incompleted "d" levels in the electronic configuration surrounding the nucleus. It apparently has the optimum number of vacancies in the fifth "d" level to establish an exceptionally strong interatomic bonding that explains, at least qualitatively, the metal's exceptional properties.

The major uses of tungsten relate not only to the special characteristics of the metal itself but also to the properties that it imparts to its compounds and

its alloys—extreme hardness, the ability to retain hardness and strength at elevated temperatures, high tensile strength, adequate electrical conductivity, and high wear resistance. The basic forms in which tungsten is consumed are, in approximate percentages, as follows: tungsten carbide, 45; alloy steels, 25; nonferrous alloys, 11; tungsten and tungsten-base alloys, 18; chemicals and others, 1 to 2. These various tungsten materials have important and in some cases very specific application in the production of metalworking machinery, tool steel, construction and mining machinery, drill bits, turbines, rocket nozzles, structural material in nuclear and space applications, transportation equipment (including tire studs), electrical equipment, lamp filaments, high-temperature thermocouples, inorganic chemicals for use in dyes, inks, glass, and luminous pigments, and other minor items. More detailed information is given by Griffith (1970).

Tungsten, because of its properties, has many uses that are basic to a modern, rapidly diversifying technology; consequently, the metal will continue to be an increasingly important, if not critical, commodity of worldwide importance. Accelerated industrial expansion and new applications predicate an increasing domestic demand for tungsten, which can be met only by discovery of new deposits, by the processing of lower-grade source materials at higher cost, by increased imports from abroad, or by the recycling of tungsten from scrap. An unsatisfactory alternative to an adequate supply is substitution of other metals for tungsten in some end-use applications. Molybdenum is substituted for tungsten in tool steels and high-temperature nonferrous alloys even though these products have a lower melting point, lower hardness at red heat, and a tendency to decarburize. Titanium carbide combined with molybdenum, nickel, or cobalt has gained acceptance in cutting tools; other materials such as aluminum oxides and industrial diamonds can be substituted in certain applications. In many lesser uses such as filaments for electric lamps no adequate substitutes are now available.

U.S. production of tungsten ore has varied widely, and although production peaks have occasionally exceeded consumption lows, the country has, on the average over the past 20 years, produced only about 75 percent of its demand. As a result, the United States is a net importer of concentrates, mostly from Canada, Australia, Bolivia, Peru, Portugal, and South Korea. Of the known and estimated world reserves approximating 220 million units WO_3 (one unit equals 1 percent per ton, or 20 pounds WO_3 containing 15.862 pounds tungsten metal), about 80 percent is estimated to be in Communist countries—60 percent in southeastern China and 20 percent in North Korea and the U.S.S.R. The impact of the Chinese reserves and potential production is the major unknown factor in predicting worldwide tungsten markets.

EXPLOITATION

Tungsten mining in the United States began on a very small scale in 1898 with production from pegmatites in Connecticut and South Dakota and from quartz veins in Arizona. The history of production from 1900 to the present has seen wide fluctuations, with short periods of high productivity stimulated by high prices during periods of national emergencies or special Government production incentive programs, followed by drastic cutbacks to lower levels. Figure 73 shows curves of production and unit price for the period 1900–1971. The three peaks on the production curve represent the effects of World Wars I and II and of the Government stockpile purchase program during the Korean War. Since 1960, annual production has fluctuated only moderately, and since 1965, it has been stabilized in the range of 400 thousand to 500 thousand units, largely as the result of the U.S. policy to sell tungsten from Government stockpiles at a fixed price.

The relation of the price to production (fig. 73) is revealing as to future domestic supplies. Three times in the past 60 years, critical demands for tungsten have been met by domestic production, which suggests that the Nation has a relatively high tungsten potential. This is not a low-cost potential, however, when compared to other producing areas in the world, nor is it an indefinite potential; but under a price incentive, tungsten can be produced in quantity. A U.S. Bureau of Mines tungsten-availability report (Larson and others, 1971) documents this situation.

The production of tungsten as a coproduct or byproduct in various mining operations is discussed later in this chapter. Such sources of supply will likely increase with the continued exploitation of large-volume, low-grade ore bodies.

GEOLOGIC ENVIRONMENT

GEOCHEMISTRY

There is a paucity of data for many aspects of the geochemical behavior of tungsten, and many of the older data (pre-1946) are probably in error because of an earlier lack of methods to analyze accurately for small amounts of tungsten in common rocks and minerals. Only in recent years have these problems been largely overcome, and data are becoming available from which a better understanding of the geo-

FIGURE 73.—United States production and price of tungsten, 1900–1971

chemistry of tungsten will emerge. The following information is based primarily on recent compilations of the geochemistry of tungsten by Krauskopf (1970) and Barabanov (1971).

Tungsten (W) is one of the rarer elements in the earth's crust. The average crustal abundance of tungsten has been estimated at 1–1.3 ppm (parts per million). Of all igneous rocks, those of granitic affinities contain the most tungsten (average 1.5 ppm). Mafic rocks have a somewhat lower range of 0.5–1.0 ppm and ultramafic rocks the lowest (0.1–0.8 ppm) (Krauskopf, 1970). Sedimentary rocks have an average tungsten content estimated at 1–2 ppm, the amount in clastic sediments generally being higher than that in carbonate rocks. The few data for metamorphic rocks are too fragmentary to substantiate any general conclusions.

Meager data suggest that the content of tungsten in natural waters is extremely low. Such low values are compatible with the general insolubility of tungsten minerals as well as with the strong tendency for any dissolved tungsten to be adsorbed on iron and manganese oxides. The average tungsten content of sea water is probably near 0.0001 ppb (parts per billion). Lakes and streams probably contain much less than 1 ppb. In acid mine waters associated with tungsten ore deposits, values are as much as 100 ppb tungsten. Exceptionally high values of 40–64 ppm tungsten are reported for the brines of Searles Lake, Calif. In hot spring waters, tungsten content may reach a few hundred parts per billion.

In general, the content of tungsten in common rock-forming minerals is low. Quartz and feldspar generally have less than 2 ppm, and mica, the rich-

est, may contain from 5 to 50 ppm. The accessory iron-oxide and titanium minerals may have tungsten values greater than 10 ppm, and the content of tungsten in niobium-tantalum minerals may reach 1 percent or more, owing to the substitution of W^{+6} for Nb^{+5} and Ta^{+5}. The hypogene manganese-oxide minerals psilomelane and cryptomelane locally contain large amounts of tungsten.

Tungsten is one of the Group VI elements in the periodic table and has atomic number 74 and an atomic weight of 184. It is a lithophile element in terrestrial environments and occurs in nature as W^{+4} (ionic radius 0.70 A) and W^{+6} (ionic radius 0.62 A). The closest relative of tungsten, molybdenum, has similar ionic radii and electro-negativities, the same valences in natural materials, and about the same abundance in the earth's crust. Other geochemically similar elements are niobium and tantalum, close neighbors of tungsten in the periodic table.

Separation of molybdenum and tungsten in natural environments occurs because of the tendency of molybdenum to form the sulfide, molybdenite, and tungsten to form the tungstates, scheelite and wolframite.

The geochemical cycle of tungsten begins with the formation of a tungsten deposit by processes related to magmatism. In a crystallizing magma, the tungsten gradually becomes concentrated in the residual fluids as either volatile compounds (not quantitatively appreciable, according to thermodynamic calculations) or soluble components of the water-rich phase. Experimental evidence indicates that tungsten is carried in ore-forming solutions chiefly as tungstate ion, tungstic acid, sodium tungstate, or a heteropoly-acid, the relative amounts of these being controlled by temperature, pH, and the silica content of the solutions (Krauskopf, 1970). At a critical stage of physical conditions and of solution and wallrock chemistry, tungsten is precipitated as either wolframite or scheelite; which tungsten mineral forms is controlled by relative amounts and activity of iron, manganese, calcium, carbon dioxide, and fluorine.

During weathering of a tungsten deposit, most of the wolframite and scheelite enter surface waters as detritus because both are fairly insoluble in the pH range of these waters. The high specific gravities and insolubilities of wolframite and scheelite predispose their accumulation in eluvial and alluvial placers from which some production has been made, but these are not a significant source of tungsten at present. The brittleness of these minerals causes them to break down during transport into very fine particles which are dispersed as fine sediment and thus lost within relatively short distances.

Narrow tungsten "halos" in soils around ore deposits suggest some mobility of the metal in near-surface waters. Secondary enrichment of tungsten is known, but is minor and very local. Alkaline solutions probably have little effect on tungsten minerals; the influence of organic matter is uncertain. Tungsten minerals are slowly attacked by acid surface waters and the released tungsten is thought to be partly dissolved as HWO_4^- and partly converted to some form of tungstic oxide (tungstite, hydrotungstite, ferritungstite). Some of the tungsten in solution may be removed by adsorption on oxides of iron and manganese. The part remaining in solution is stable as polytungstate ions such as $6H(WO_4)^-$ and $(HW_6O_{21})^{-5}$ and heteropolyacids such as $H_8Si(W_2O_7)_6$ having silicon as the central atom in the complex. The concentration in natural waters is generally very low. Much of the tungsten is eventually dispersed in sedimentary rocks in amounts about the same as in igneous rocks. Enrichment may occasionally occur in ferruginous sandstone and shale. In soils tungsten is slightly enriched in the B horizon or lower A horizon and may form halos around ore deposits.

Almost nothing is known about the biogeochemistry of tungsten. Some indication of enrichment in plants in mineralized zones has been documented. There is little information on black shales, but high values for graphitic phyllites and schists in Uganda, Ruanda, and India suggest a syngenetic sedimentary origin of the tungsten and a correlation with carbon content. An important biogeochemical role is unlikely, since tungsten in more than traces is poisonous to most organisms.

The behavior of tungsten in metamorphic processes is unknown. It has been speculated that tungsten occurring in minute amounts in ordinary rocks may be mobilized by fluids generated during metamorphism and transported long distances to be deposited where the solutions change character. Thus, some investigators have suggested that most tungsten deposits, even those intimately associated with granites, are derived by metamorphic processes from the small accumulation of tungsten in sediments.

MINERALOGY

Although more than 20 species of tungsten-bearing minerals are known, only members of the wolframite group and scheelite are important as ore minerals. Many are very rare in occurrence and several have been described from only one locality. Only the more common minerals are listed in table 145.

In many deposits throughout the world, tungsten occurs with minerals of other commodities. In the

TABLE 145.—*Minerals of tungsten*

Name	Composition	Relative abundance
Wolframite group:		
Huebnerite	$MnWO_4$	Common.
Wolframite	$(Fe,Mn)WO_4$	Major.
Ferberite	$FeWO_4$	Common.
Scheelite	$CaWO_4$	Major.
Powellite	$Ca(Mo,W)O_4$ (WO_3 to about 10 percent)	Common.
Stolzite	$PbWO_4$	Uncommon.
Tungstite	H_2WO_4	Common.
Cuprotungstite	$Cu_2WO_4(OH)_2$	Uncommon.

principal tungsten mine in the United States, the tungsten is a coproduct with molybdenum and copper; but in the second largest producer, tungsten is a byproduct of molybdenum mining. Ore minerals of other commodities that commonly occur in the tungsten deposits of the world are molybdenite (MoS_2), cassiterite (SnO_2), chalcopyrite ($CuFeS_2$), bismuthinite (Bi_2S_3), native bismuth (Bi), and fluorite (CaF_2). In a few places in the United States, tetrahedrite ($3Cu_2S \cdot Sb_2S_3$) and sphalerite (ZnS) are coproducts.

TYPES OF DEPOSITS

Concentrations of tungsten occur in a wide variety of geologic environments that range from high-temperature, deep-seated deposits to those deposited at the surface from relatively low-temperature hot springs. In addition, tungsten has been recovered from placers and is known to exist in significant though as yet-uneconomic amounts in the brines of Searles Lake, Calif. The principal types of occurrence from which most production has come are contact-metamorphic deposits (tactites), hydrothermal veins, and stockworks and related porphyry-molybdenum deposits. Other deposits that have been productive or represent significant resources either are variants of these major types or result from special geologic situations. These include pegmatites, iron-manganese-bearing hot-spring deposits, replacements of various host rocks under special conditions, placer deposits, and the Searles Lake brines.

CONTACT-METAMORPHIC DEPOSITS

Tactite, one of the products of contact metamorphism, is the principal commercial source of tungsten in the United States and is second only to quartz veins as a commercial source on a worldwide basis. Tactites are the products of high-temperature replacement and recrystallization of pure or impure limestone or dolomite at or near the contact of intrusive igneous rocks. The resulting dark-colored deposits, comprising various combinations of such dark calc-silicate minerals as garnet (usually almandine or andradite), epidote, hedenbergite, and hornblende, together with magnetite and some quartz and calcite, are usually conspicuous in contrast to the lighter-colored granitic rocks or the sedimentary sequence into which the granite was intruded. The name "tactite" was applied to deposits of this type by Hess (1919) and is analogous in a broad sense to the Swedish term "skarn."

Contact-metamorphic deposits have been produced by two basic processes—simple thermal metamorphism of impure carbonate strata, and additive metamorphism of either pure or impure carbonate layers wherein at least part of the material essential to the deposit is added from the magma. Presumably, both processes are active in the formation of tactites, and essential materials added are principally iron and silica with lesser amounts of aluminum manganese, and possibly some magnesium. Locally, significant amounts of tungsten, molybdenum, copper, zinc, sulfur, and fluorine are added—usually at a late stage. Determination of which major elements have been added and in what amounts is often difficult unless the tactite zone can be traced along strike into the unaltered strata where the original composition can be determined. However, the presence of one or more of the metallic elements, and of sulfur, fluorine, or boron, is considered to be indicative of additive processes.

Tungsten, where introduced into tactites, occurs only as scheelite or molybdenum-bearing scheelite. Magnetite is usually present and may be abundant as at the Long mine, Pershing County, Nev., and the Old Hickory mine, Milford County, Utah. Pyrite, pyrrhotite, molybdenite, sphalerite, chalcopyrite, tetrahedrite, stibnite, and bornite are formed at a late stage in some deposits, and fluorite, usually present, is locally abundant as at Darwin, Calif., and Tem Piute, Nev.

In most places, tactites form distinctive, sharply bounded bodies whose shape and distribution are controlled by many factors but mainly by the contact of an intrusive body which usually forms one wall, by favorable composition of the invaded host rock, and by the structural relations of the strata to the contact. Tactite developed along conformable contacts tends to form tabular bodies parallel to the contact that seldom maintain a uniform width and vary from a few inches to many feet. Where a contact crosses bedding, beds more favorable lithologically may be replaced outward from the contact for greater distances than less favorable ones—in some instances for more than a thousand feet. Steep beds may be replaced for considerable vertical extent, the tactite

pitching along the intersections of favorable beds with the intrusive. In some places, as at Tem Piute, Nev., ore-bearing tactite having no exposed contact with igneous rock has formed in layers parallel to a contact but is separated from it by several hundred feet of barren strata. Irregularities in igneous contacts and premineralization faults provide traps as well as channelways for mineralizing solutions that result in major local enlargements of tactite bodies. At the Pine Creek mine, Calif., and at the Nevada Scheelite mine, Mineral County, Nev., overhangs of the granite contact are associated with enlarged and enriched ore bodies. Also at the Pine Creek mine, as at the Riley mine in the Osgood Range, Humboldt County, Nev., plunging troughlike curvatures of the intrusive contact are occupied by enlarged ore shoots. Roof pendants and inclusions of calcareous sedimentary rocks in plutonic rocks may be converted to tactite bodies that range in size from only a few feet in all dimensions to others that measure hundreds of feet. Large pendants like the one at Pine Creek, Calif., which is 7 miles long and nearly a mile wide, contain a variety of rock types, only some of which are replaced by tactite.

Scheelite is seldom uniformly distributed in tactite, and many tactite bodies, perhaps most, contain none at all. In many mines, scheelite occurs in fairly well defined shoots or is more concentrated along certain bands in the tactite than in others. The vertical range may be as great as that of the tactite itself or may be restricted by such factors as permeability, fracturing, channeling of the ore-bearing solutions, and other local controls.

Scheelite-bearing tactite deposits range in size from small isolated pods scattered along a contact to massive bodies which may comprise millions of tons. The content of WO_3 in tactite deposits is generally low. Parts of the Humboldt ore body at Mill City, Nev., contained 10 percent WO_3 but the entire body averaged about 1 percent. A few smaller mines in California and Nevada yielded ore averaging between 1 and 2 percent, but these are the exception. Most productive mines contain between 0.5 and 1.0 percent and a few properties, during periods of high prices and under conditions of inexpensive mining, produced concentrates from tactite containing as little as 0.3 percent WO_3.

Major production of tungsten from tactite deposits in the United States has come from the Pine Creek mine, Inyo County, Calif. (Bateman, 1965; Gray and others, 1968); the Mill City district, Pershing County, Nev.; various deposits in the Osgood Range, Humboldt County, Nev. (Hobbs and Clabaugh, 1946; Hotz and Willden, 1964); and the Brownes Lakes and Calvert Creek deposits in Beaverhead County, Mont. Numerous other deposits, particularly in the Sierra Nevada of California and in western Nevada, have produced lesser but cumulatively very significant amounts of concentrates.

Major occurrences of tungsten-producing tactite outside the United States occur at the Flat River area in the Northwest Territories, Canada, on King Island, Tasmania, and in South Korea.

TUNGSTEN-BEARING VEIN DEPOSITS

Tungsten-bearing quartz veins are widely distributed and account for more than three-fourths of the known world reserves of the metal. The great bulk of these reserves, however, are concentrated in the extensive tungsten province of southeastern China. As with the tactite deposits, most of the productive veins are associated spatially and probably genetically with plutonic rocks of granitic composition and usually occur near their contacts—either within border zones of the plutons or, more generally, in the adjacent intruded terrane. In contrast with environments favorable for tactites, however, the host rock associated with such veins generally contains little, if any, carbonate. Shale, siltstone, and quartzite or their metamorphic equivalents, as well as igneous rocks, either older than the parent intrusive or forming the border zones of the parent intrusive itself, are favorable hosts for the deposition of tungsten in quartz veins. Exceptions to this general rule are the quartz-scheelite veins cutting carbonate beds in the Minerva district, Nevada, and calcite-scheelite veins and stockworks in the Cherry Creek district and the Snake Range, Nev.

Most tungsten veins are mineralogically simple and consist of quartz with scheelite and (or) one of the wolframite series and minor amounts of other minerals. Scheelite is the only ore mineral in the quartz-calcite veins at Atolia, Calif., which occur in quartz monzonite, and at the Minerva district, Nevada, where veins cut carbonate beds. Ferberite is the predominant mineral in veins of the famous Boulder tungsten district, Colorado, which carry only minor amounts of scheelite. Huebnerite is the dominant mineral at the Ima mine, Idaho, and at the Hamme district, North Carolina, although some scheelite occurs in both places. In some veins both scheelite and wolframite occur in nearly equal amounts. Other minerals such as sphalerite, galena, chalcopyrite, tetrahedrite, and arsenopyrite occur in large enough amounts in some deposits to be recovered as byproducts. Pyrite, pyrrhotite, molybdenite, fluorite, rhodochrosite and some feldspar may be present as gangue minerals. In many dis-

tricts quartz veins that are mined primarily for other metals—especially gold—contain scheelite as a sporadically distributed secondary component. The Mother Lode of California, the Murray district, Idaho, and the Jardine district, Montana, are examples.

Tungsten-quartz veins are similar in most respects to typical hydrothermal vein deposits. They are tabular bodies that vary greatly in length, width, and depth. Although some vein zones extend for thousands of feet, the individual component veins tend to pinch and swell or to be arranged as a series of echelon lenticular segments both along strike and downdip. The attitude of the veins depends largely on the local structural environment. Most known occurrences tend to dip steeply, but a few are controlled by nearly flat joint systems in igneous terrane.

Tungsten minerals in veins are usually localized in ore shoots. These shoots, as well as the veins themselves, are controlled by general factors of temperature, pressure, chemical composition of mineralizing solutions, available channelways for solutions, the sequence of mineral formation, and the local effect of structure and type of country rock. Quartz-tungsten veins are, as a rule, spatially very closely related to the contacts of igneous intrusive rocks and notably to the roof zones of such intrusions. This relation is illustrated by the not-uncommon association of major districts with small plutons as at Boriana, Ariz., and the Ima mine, Idaho, which are probably in cupolas of larger subjacent masses, and the alinement of major vein zones with granite-cored anticlinal ridges as in the Chinese deposits. Tungsten ore shoots in quartz veins range from small isolated pockets of scheelite or wolframite to nearly continuously mineralized vein material that may measure a thousand feet or more on strike and downdip. Such extensive ore shoots are the exception in the United States, however, and most individual shoots have a vertical range of less than 500 feet. Cumulatively, the echelon ore bodies both at the Ima mine, Idaho, and in the Hamme district, North Carolina, extend well beyond a depth of 1,000 feet. In most occurrences, however, the ore shoots are small and even though the vein itself may be extensive, the concentrations of tungsten minerals within it are widely and erratically dispersed. Such "pockety" habit is commonplace and makes exploitation difficult. The thickness of tungsten veins varies as widely as do length and depth, but the economically minable size depends as much on grade, attitude, and other physical factors as on actual extent. For example, a 1-inch-thick vein of pure ferberite (60 percent WO_3) in the Boulder district, Colorado, was mined; elsewhere, shoots averaging less than 1 percent across 15 feet or more of vein material have been worked. The average grade for all productive tungsten vein deposits in the United States is probably close to 1 percent. Major productive vein deposits in the United States are at Boriana, Ariz., Atolia, Calif., Boulder district, Colorado, Ima, Idaho, and Hamme, North Carolina. Numerous smaller deposits are widely scattered in Arizona, Nevada, Colorado, Washington, Idaho, and Montana.

STOCKWORK AND RELATED DEPOSITS

Deposits of tungsten minerals as fracture fillings and replacements in stockworks and breccia zones are known at several places in the United States. These occurrences, though comprising varied host rocks, mineral associations, shape, size, and grade, have at least two common prerequisites of origin—a source of hydrothermal solutions with suitable access channelways, and suitable sites of deposition prepared through intimate fracturing, brecciation, or shearing of the host terrane. In most deposits of this kind (except the closely related porphyry-molybdenum occurrences), scheelite is the only tungsten mineral. Where breccias and stockworks were formed in carbonate rocks, the composition of the host undoubtedly was a major factor in the deposition of the scheelite. Similar chemical controls may have been an important, even if subordinate, factor in other environments.

At Henderson Gulch, Mont., parts of a highly fractured granitic body are mineralized along fracture planes by iron sulfides with some gold and scheelite. A small amount of gold and scheelite has been recovered from placer deposits downstream from this occurrence although the source rock itself has so far proved to be too low-grade for mining. At the Goat Creek property near Thompson Falls, Mont., an elliptical area of moderately fractured and altered nearly horizontal sedimentary rocks of the Wallace Formation of the Precambrian Belt Supergroup carries thin seams and veinlets of iron sulfides, molybdenite, and some scheelite. This occurrence, located on the crest of a broad anticline, coincides with a strong, nearly circular aeromagnetic anomaly that has been interpreted to reflect a buried stock at some unknown depth. Although this deposit has not yet been proved economically feasible, it illustrates a mode of occurrence that may have future potential either here or elsewhere.

Small calcite-scheelite replacement pipes and stockworks have been mined in Nevada and Cali-

fornia. These deposits, though locally high grade, are small and appear to be related to more extensive vein deposits in the same area.

Huebnerite occurs in small amounts disseminated through large volumes of the porphyry-molybdenum ore body of the Climax Molybdenum Co. at Climax, Colo. Although the grade of the tungsten is only a few hundredths of 1 percent and thus is far below the economic cutoff for tungsten alone, the huebnerite is recovered as a byproduct of the very large scale mining for molybdenum and has become a very significant source of domestic supply; in 1970, Climax was second only to Pine Creek, Calif., in United States production of tungsten. The geologic evolution of the Climax stock and the sequence of mineralization are extremely complex and have been well documented in the literature (Wallace and others, 1968). The composite Climax stock was intruded into Precambrian schist and gneisses and comprises four separate intrusions, each of which had its own associated hydrothermal event. The first three of these produced large stockwork ore bodies and associated alteration zones that cap and flank each intrusive body. The positioning of these separate intrusions in the same area has led to much overlapping and juxtaposition of ore zones. Each mineralizing episode, however, produced a generally consistent pattern of ore distribution with a molybdenum-rich zone overlain by a zone with low molybdenum but anomalous amounts of huebnerite and pyrite. The upper, currently producing molybdenum ore body is overlapped by one of the tungsten-bearing halos.

The Climax deposit is the only one of this kind in the United States from which byproduct tungsten is recovered. However, the reported association of tungsten minerals with geologically similar deposits, not only in Colorado but also in New Brunswick, Canada, raises the potential for this type of occurrence to become an increasingly important source of future supply.

OTHER MODES OF OCCURRENCE

Pegmatites containing scheelite or wolframite or both are found in many parts of the world, and in many places are closely associated with tungsten-bearing quartz veins near the contacts of intrusive bodies. For the most part, the deposits are small and because of their irregular and generally pockety nature are difficult to exploit. A relatively insignificant percentage of the world production has come from pegmatites. The only important tungsten-bearing pegmatites in the United States, those at the Oreana mine, Pershing County, Nev., were largely mined out in the 1940's. Other occurrences with very minor production are in the southern Black Hills of South Dakota and at Silver Hill near Spokane, Wash.

The mushroom-shaped scheelite ore body of the Yellow Pine mine, Idaho, was a replacement of brecciated quartz monzonite near a major shear zone (Cooper, 1951). The gangue comprised crushed country rock replaced by fine orthoclase and quartz. Early-formed gold, pyrite, and arsenopyrite were followed by scheelite and subsequently by stibnite with some silver. This ore body, which produced about 826,900 units WO_3 during 1941–45, has been mined out.

The replacement of a bed of sandy dolomite in the northern Black Hills of South Dakota by wolframite accompanied by gold, barite, and a little scheelite and stibnite is apparently unique in the United States (Runner and Hartmann, 1918).

Several manganese- and iron-oxide deposits of hot-spring origin in the Western United States contain significant amounts of tungsten in a form still unidentified but apparently closely associated with the oxide minerals. These deposits, formed at or very near the surface, comprise various mixtures of manganese and iron oxides in surficial alluvial materials, as hot-spring aprons, or as near-surface veins. Only the large deposits at Golconda, Nev., where tungsten-bearing oxides impregnate Pleistocene continental fanglomerate, contained enough tungsten to be exploited (Kerr, 1940).

Anomalous amounts of tungsten have been reported from other hot-spring deposits as well as from epithermal manganese-bearing veins in Nevada, Oregon, New Mexico, and Bolivia. Many others probably exist, but because of their usual small size and the metallurgical problems they pose, they will probably always represent a very small part of world resources.

Commercial concentrations of tungsten minerals in stream placers are rare and are generally restricted to areas close to abundant coarse-grained source material as in the Atolia-Randsburg district, California. A small amount of fine-grained scheelite was recovered as a coproduct with gold from placers that were dredged for several miles in Henderson Gulch, Mont., downstream from the mineralized stockwork deposit previously described. Small amounts of wolframite have been recovered from eluvial material in the Germania district, Stevens County, Wash.

Significantly larger amounts of placer tungsten are reported to have been recovered from eluvial and stream placers in the great Chinese tungsten

province and from the extension of this province into Indochina.

A small but anomalous amount of WO_3 is present in the saline brines of Searles Lake (Carpenter and Garrett, 1959) and, to a lesser extent, in Owens Lake, both of which are a part of the Pleistocene Owens River interior drainage system in eastern California. The drainage area includes the eastern slope of the Sierra Nevada and the tungsten deposits of the Bishop region—from which much of the tungsten in the brines was probably leached. Numerous springs, at least one of which is known to carry anomalous amounts of tungsten today, may also have contributed to the total tungsten that collected in the lakes at the time of the throughgoing Pleistocene drainage.

Tungsten in Searles Lake occurs as a solute, probably as a complex ion, in the brines in the amount of about 0.007 percent (70 ppm) WO_3. Although the amount is low, and no efficient extraction method has yet been designed, these brines must be considered a major resource for future consideration, because the large volume of brines contains approximately 8.5 million units WO_3—more than half the known reserves of the United States.

RESOURCES

IDENTIFIED AND HYPOTHETICAL RESOURCES

Reserves of tungsten in the United States are estimated to be nearly 15 million short ton units WO_3 in ore containing more than 0.3 percent WO_3. This is about 6.5 percent of an estimated world reserve total of 230 million units. Nearly two-thirds of the U.S. reserves occurs as scheelite in tactite deposits located principally in California, Nevada, and Montana. Other tactite occurrences are located in Utah, Arizona, Washington, and Idaho. Most of the remaining one-third of the reserves is found as ferberite, wolframite, and huebnerite in quartz veins in Arizona, Idaho, Colorado, and North Carolina and as huebnerite in the Climax porphyry-molybdenum deposit of Colorado.

An illuminating aspect of the resource potential for tungsten in the United States is the fact that since 1955 the total United States reserves have remained stable or have increased significantly—especially in recent years. This has occurred in spite of the very high rate of production in the mid-1950's and the industry's relatively depressed condition since then. Presumably this fact reflects new discoveries during periods of active exploration and exploitation as well as significant extension of reserves in the few major mines that have produced more or less continuously.

In addition to its reserves, the United States has numerous deposits containing less than 0.3 percent WO_3 that may be considered as conditional resources. Most of these resources are in tactites and stockworks, and they are estimated to total two to three times the known U.S. reserves. The 8.5 million units WO_3 in Searles Lake brines is an additional conditional resource.

An extrapolation of identified resources into the realm of hypothetical ore bodies may reasonably be attempted on the basis of our knowledge of regional distribution, modes of occurrence, and geochemical association. Those parts of the Western United States from which most of our tungsten has been produced include vast areas covered by surficial debris and Tertiary sedimentary or volcanic rocks that undoubtedly conceal deposits at least equal in volume to, if not greatly exceeding, known deposits. Also, the proved association of important amounts of tungsten with molybdenum in porphyry-molybdenum deposits presages the discovery of others of this type, especially in Colorado. No real measure of tungsten recovery from this source in other parts of the country is yet available, but because of the tremendously large molybdenum resources estimated for deposits of this kind, the potential for tungsten byproduct recovery is proportionately large.

More than 90 percent of the world's known tungsten reserves are outside the United States, with 60 percent in southeastern China. Table 146 summarizes the general reserve estimates and geologic characteristics of the major tungsten-producing countries of the world. Reserve figures are estimates only, and those for Communist countries, where information is outdated, inadequate, and difficult to evaluate, are far less reliable than those for the free world.

SPECULATIVE RESOURCES

The worldwide pattern of tungsten distribution, combined with the known geologic conditions related to its localization, leads to broad speculation of ultimate potential which can reasonably be extended an order of magnitude beyond the identified and hypothetical world resources.

The localization of many of the major tungsten districts of the world in a broad circum-Pacific belt extending from South America through the United States, Canada, Alaska, and down the eastern coast of Asia into Australia and Tasmania, marks this zone as one in which other deposits or districts may very likely be found. The discovery and extensive production from contact-metamorphic deposits in

TABLE 146.—*Geology and reserves of principal tungsten deposits of the world*

Country	Reserves [1] (millions of short ton units WO_3)	Major deposit types	Tungsten minerals (major mineral italized)	Major associated minerals of other commodities	Host rocks	Associated igneous rocks	
						Classification	Age
North America:							
Canada	30.0	Contact metasomatic.	Scheelite	Chalcopyrite	Paleozoic limestone.	Quartz monzonite.	Cretaceous.
United States	15.0	Contact metasomatic, stockwork veins, quartz veins.	*Scheelite*, wolframite, ferberite, huebnerite.	Molybdenite, chalcopyrite.	Limestone, granitic and metasedimentary rocks.	Quartz monzonite to granite.	Late Paleozoic, Jurassic to Cretaceous, Tertiary.
South America:							
Bolivia	5.5	Quartz veins	*Wolframite*, scheelite.	Cassiterite, sphalerite, stannite, chalcopyrite, fluorite, bismuth minerals.	Paleozoic sedimentary rocks, Cretaceous to Tertiary sedimentary and volcanic rocks.	Dacite to quartz latite.	Late Jurassic, late Tertiary.
Brazil	2.5	Contact metasomatic, quartz veins.	*Scheelite*, wolframite.	Molybdenite, bismutite.	Precambrian calcareous rocks in mica schists.	Granite	Precambrian.
Europe:							
Portugal	1.4	Quartz veins	*Wolframite*, scheelite.	Cassiterite, chalcopyrite, sphalerite, galena, fluorite.	Granite and metamorphic rocks.	----do	Late Paleozoic.
U.S.S.R.	30.0	Contact metasomatic, quartz veins.	*Scheelite*, wolframite.	Molybdenite, powellite, bismuth minerals, fluorite, cassiterite, sulfides.	Various metasedimentary rocks.	----do	Late Paleocene to Eocene.
Asia:							
Burma	4.4	Quartz veins	*Wolframite*, scheelite.	Cassiterite, minor sulfides.	Sedimentary rocks.	----do	Mesozoic(?).
China	132.3	----do	Wolframite	Cassiterite, bismuth minerals, molybdenite, chalcopyrite.	Paleozoic and Mesozoic sedimentary rocks and granite.	----do	Late Jurassic.
North Korea	15.7	----do	*Wolframite*, scheelite.	Chalcopyrite, fluorite.	Phyllite, mica schist, gneiss.	----do	Cretaceous.
South Korea	6.4	Contact metasomatic, stockwork veins, quartz veins.	*Scheelite*, wolframite.	Molybdenite, chalcopyrite.	Metasedimentary rocks and granite.	----do	Do.
Malaysia	2.0	Quartz veins, contact metasomatic.	*Wolframite*, scheelite.	Cassiterite, minor sulfides, fluorite.	Paleozoic and Mesozoic sedimentary, volcanic, and metamorphic rocks.	----do	Mesozoic.
Australia	4.8	Contact metasomatic quartz veins.	Wolframite, scheelite.	Cassiterite, molybdenite, bismuth minerals, fluorite.	Sedimentary, metasedimentary rocks and granite.	----do	Late Paleozoic.

[1] Identified deposits from which minerals can be extracted profitably with existing technology and under present economic conditions.

the Yukon within the last 20 years is a specific example. In other parts of the world, tungsten, presumed to be of Precambrian age, is widely scattered in parts of the Brazilian, African, and Canadian Shield areas, as well as in the Precambrian crystalline cores of the Rocky Mountains of Colorado and Wyoming. Although mostly small as now known, these deposits are indicative of a time-and-place relation that once thoroughly understood might lead to the discovery and exploitation of significant amounts of tungsten ore. The association of tungsten with porphyry-molybdenum deposits in Colorado is well known and such association is suggested in other areas as well. In contrast, the association of tungsten with porphyry copper deposits is thought to be rare or is undetermined, in spite of the fact that these deposits are strikingly similar in mode of occurrence and origin to the molybdenum-bearing porphyries. Recovery of tungsten as a byproduct from some of the porphyry copper operations is a speculative possibility.

PROSPECTING TECHNIQUES

Many early discoveries of tungsten deposits were made from the recognition of scheelite and wolframite, accompanying other heavy minerals, in panned concentrates collected in the search for gold and other precious metals. In outcrop, wolframite, as black bladed crystals in quartz veins, was easily identified, but scheelite, because of its similarity in color and luster to quartz and feldspar, was often overlooked. Panning is still a very useful technique for tracing tungsten to its source. Development of a portable shortwave ultraviolet light during the 1930's greatly stimulated the search for scheelite, which fluoresces a bright blue-white to creamy-yellow at this wavelength. The degree of yellow fluorescence is controlled by the amount of molybdenum in the mineral structure. A person experienced in the use of this technique can detect very

small amounts of scheelite and estimate grade quite accurately. Most discoveries of workable tungsten-bearing tactite deposits in the United States were made by use of this method through systematic scanning of recognized tactite zones.

Geophysical methods are particularly applicable to the selection of geologic environments in which tungsten deposits might logically exist, but no direct measurements of the tungsten content can be made by these techniques. Broad regional studies by means of airborne magnetic and radiometric surveys and regional gravity measurements are useful in identifying variously anomalous rock bodies that are known to relate to possible environments of ore deposition. Such measurements have located igneous contacts, have provided data on location and depth of buried plutons and cupolas, have delineated tungsten-associated granites (as in the Kazakhstan region of the U.S.S.R.) that have relatively low magnetic field intensity and high radioactivity, and have helped define such regional structures as the Colorado Mineral Belt, whose intrusive igneous masses are reflected in low gravity anomalies even though the associated molybdenum-tungsten mineralization is not so reflected.

Detailed geophysics may apply directly to the detection of ore zones, individual ore bodies, or promising environments. Many tactites that contain magnetite and (or) pyrrhotite are responsive to magnetic methods of detection; those with high sulfide contents respond to various electrical techniques; and detailed gravimetry may usefully refine the location, size, and depth of small plutons or the configuration of significant contacts.

Geochemical surveys, though used sparingly in the United States to date, can be useful for future tungsten exploration. The simplest and perhaps most useful technique is the panning and analysis of stream sediments. Because of their high specific gravity and low solubility, tungsten minerals tend to concentrate as resistate fractions in streambeds, and the systematic sampling of stream sediments will often identify anomalous drainage basins and pinpoint source areas. The sampling and analysis of individual plutons of an intrusive complex has shown that, in some instances, plutons associated with tungsten mineralization contain anomalous amounts of tungsten and associated elements. This technique, even though not specific for individual deposits, does narrow the target for the application of other methods.

Tungsten, because of its low chemical mobility under weathering conditions, generally produces geochemical anomalies of only limited range surrounding the source material. Analysis for indicator elements such as fluorine, arsenic, and (or) phosphorus that have greater mobility and are commonly associated with tungsten deposits may, in some circumstances, be more useful because of the wider halos they produce in rocks, soils, and (or) plants. In some special circumstances, other metallic elements commonly associated with tungsten such as molybdenum, copper, bismuth, antimony, and tin, may be used as indicators.

PROBLEMS FOR RESEARCH

Much has been learned about tungsten deposits from long experience with them. The application of empirical data has identified the common modes of occurrence, the effects of local geologic controls, the general geologic environment, associated minerals, general distribution, and other characteristics, and it has been useful in the discovery of new deposits and even new districts. There are limits, however, to this approach and a full evaluation of the resource potential of tungsten must await the answers to many basic questions: Why is tungsten found in some geologic provinces and not in others? Why is it associated with igneous rocks of certain composition or of certain ages? Why is it frequently pockety and erratic in distribution? Why has it been deposited over such a wide range of temperature-pressure conditions? Why is it deposited as scheelite in one place and wolframite in another? These are but a few questions, most of which relate to tungsten's geochemistry—its distribution in the earth's crust and the processes by which it is concentrated into ore deposits.

Answers to these and other pertinent questions can come only from basic research that should, ideally, combine geologic mapping and sampling of carefully selected field areas with detailed laboratory work on the mineralogy and chemistry of all related geologic components. One of the key restraints in this approach has been the inability to analyze with accuracy for small amounts of tungsten (less than 10 ppm) in rocks and minerals. It is hoped that the refinements in techniques already made or being developed will lower the level of accurate detection into the parts-per-billion range. Such refined measurements may lead, for example, to the identification of source rocks, the delineation of channels of migration of ore-bearing solutions, or the recognition of dispersion halos of buried ore bodies.

Many prospecting techniques have been used in the search for tungsten, but new approaches are needed and undoubtedly will be developed. Immediate help

is available, however, through the more imaginative use of known techniques especially for the identification of favorable environments in covered areas. Intensive application of various geophysical methods to locate contact zones or buried stocks and cupolas, with which many tungsten deposits are associated, is an approach that should prove fruitful.

Technological problems in recovery of tungsten from ore have been as varied as the modes of occurrence. Where ore minerals are coarse grained and the gangue has low specific gravity, the problem is minimal; in tactites where the gangue minerals are nearly as heavy as the ore minerals, recovery is more difficult and still inefficient; in special occurrences, as at Golconda, expensive chemical processes must be used that can recover only a part of the contained metal; and for some occurrences, as at Searles Lake, no economic process has yet been devised for recovery. Most of the scheelite recovered from tactite deposits contains several percent calcium molybdate (powellite) in its molecular structure, and for many uses, the scheelite must be purified by chemical treatment to remove the molybdenum. Byproduct recovery from very low grade material is usually extremely inefficient, and new techniques to improve such recovery may also be applicable to the recovery of much of the tungsten that has been lost or is still being lost in the tailings piles of tungsten mills.

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VANADIUM

By R. P. Fischer

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ABSTRACT OF CONCLUSIONS

Vanadium is used mainly as an alloy agent in steel. Its domestic consumption increased rapidly during the 1960's, and a growth rate of demand higher than that of any other ferrous mineral has been predicted to the year 2000. Foreign uses, consumption, and predicted requirements have a similar pattern.

Predicted domestic requirements to the year 2000 exceed the estimated amount of vanadium available from productive domestic sources by about 300,000 to 400,000 short tons. Domestic resources in magnetite deposits and in carbonaceous shales are adequate to furnish this deficient vanadium, but they can do so only if domestic metallurgical practices are modified or new ones are developed.

Foreign reserves in productive titaniferous magnetite deposits and resources in known but unproductive deposits of this type are adequate to satisfy world requirements for vanadium in the foreseeable future; these deposits occur in many countries, but the largest are in Australia, Canada, South Africa, and the U.S.S.R. Large resources also occur in vanadiferous shales in various parts of the world; those in Australia and the U.S.S.R. are perhaps more apt to become productive. Small but significant amounts of vanadium will be recovered from other iron ores, phosphate rock, petroleum residues, and other byproduct sources.

Although vanadium resources are large, vanadium supplies large enough to satisfy requirements are not necessarily secure, because so much vanadium is recoverable only as a byproduct of operations for other commodities.

INTRODUCTION

Vanadium (V) has the atomic number of 23 and the atomic weight of 50.95. It is a bright silver-white to steel-gray metal, with a melting point of about 1,900°C. Its specific gravity is 5.87 at 15°C. It alloys with several other metals.

About 80 percent of the vanadium consumed domestically has been used as an alloy in steel (fig. 69); foreign usage is similar. Vanadium is added mainly to toughen and strengthen steel and to control its grain size (National Materials Advisory Board, 1970; Busch, 1961; Griffith, 1970). In vanadium-bearing tool steels, the amount used ranges from about 0.5 to 4 percent V, and it is commonly used in varying com-

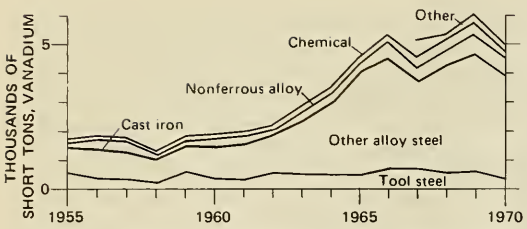

FIGURE 74.—Principal uses of the vanadium consumed in the United States, 1955–70. Data from U.S. Bureau of Mines "Minerals Yearbook" published annually.

binations with chromium, niobium, molybdenum, nickel, and tungsten; a limited degree of substitution among these metals is possible but not usually practiced. The class "Other allow steels" shown in figure 74 mainly comprises the "high strength-low alloy steels" (HSLA) that are used principally for high-pressure pipelines and construction purposes; the use of this type of steel, and the consumption of vanadium in it, has increased appreciably since the early 1960's. Generally, only 0.02–0.1 percent V is used in most of these steels, but it increases the yield point from about 35,000 psi (pounds per square inch) to the range of 50,000–65,000 psi. Niobium is used with vanadium in some of these HSLA steels, and it can be substituted for vanadium to a considerable extent if desirable from the standpoint of price or supply of these two alloy metals; other alloy metals can also be used with vanadium or as substitutes for it in some steels. A small amount of vanadium is used, along with other alloying metals, in cast irons made for special purposes. In the future an appreciable increase in the use of vanadium in the continuous casting of steel billets is possible but not likely; in this practice, vanadium is used along with, or partly in substitution for, aluminum and (or) niobium.

Vanadium as an alloying agent in nonferrous metals is used chiefly with titanium in the aerospace field, an application that is expected to increase significantly in the future. Vanadium has numerous uses in the chemical industry, especially as a catalyst. Vanadium metal, with several other metals added as alloys, is a candidate for use in the nuclear industry as a fuel-cladding material for advanced liquid-metal-cooled fast-breeding reactors; other candidates for this application are stainless steels and molybdenum- and cobalt-base alloys. If vanadium is ultimately selected, vanadium requirements after about 1985 would be large.

From the 1940's until about 1960, the United States was the world's principal producer of vanadium, and it enjoyed a moderate export market. In recent years, domestic production has remained fairly constant, at about 6,000 short tons V yearly, but consumption has increased and now about equals production; some exporting has continued but is about equaled by imports. Future domestic requirements are expected to increase appreciably (National Materials Advisory Board, 1970). Griffith (1970, table 2) predicted domestic demand in the year 2000 to range from 25,500 to 37,500 short tons V, projected on the basis of an estimated growth rate of demand higher than that of any other ferrous mineral. (For comparative figures of the predicted growth rate of demand for the ferrous minerals see table 1, p. 245, U.S. Bureau of Mines (1970).) Using this predicted growth rate of demand, Griffith (1970) estimated cumulative domestic requirements in the 1968–2000 period to range from 420,000 to 520,000 short tons V; he also estimated known reserves in productive domestic sources to total only 115,000 short tons of recoverable vanadium, which indicates an appreciable domestic deficiency. New domestic sources will have to be developed or imports increased to meet this deficiency.

PRODUCTION

GEOGRAPHIC SOURCES OF VANADIUM

Figure 75 is a generalized graph showing vanadium production for every tenth year from 1910 to 1970. A limited and probably desultory U.S.S.R. production in the 1930's and 1940's is not plotted. Other countries are known to have produced vanadium, but production figures are generally not available, and a category of "other" is not shown on the graph. In 1970 this "other" production probably amounted to 1,000–2,000 short tons V, most of which came from Canada, Chile, several European countries, and Japan. This "other" category was not significant in earlier years except during World War II, when Germany and Japan recovered appreciable vanadium, probably in the order of 3,000 short tons V yearly for a few years.

GEOLOGIC SOURCES OF VANADIUM

Figure 76 is a generalized graph showing the geologic types of deposits that yielded the vanadium production shown in figure 75. The category "Sandstone and others" represents vanadium production in the United States; about 90 percent of the total U.S. production during 1910–70 is from sandstone deposits, a very small part from vanadate ores, and the

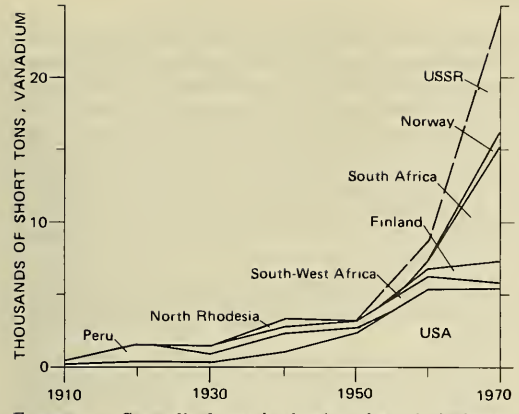

FIGURE 75.—Generalized graph showing the principal geographic sources of vanadium, 1910–70. Data from published figures of U.S. Geological Survey (1910 and 1920) and U.S. Bureau of Mines, except U.S.S.R. data for 1960 and 1970, which are estimates by the writer.

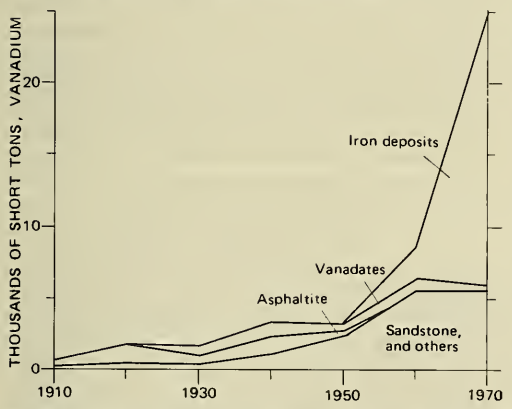

FIGURE 76.—Generalized graph showing the principal geologic types of deposits from which vanadium was recovered, 1910–70. Compilation by author, based on data in figure 75.

rest is from phosphate rock and the deposit in Arkansas described below. The category "Iron deposits" is wholly from titaniferous magnetite deposits. The vanadium produced in 1970 from countries other than those shown in figure 75 (see "Geographic Sources of Vanadium") was derived from iron ores, the residue of petroleum refining, the soot and ash from furnaces burning crude oil, the sludge derived from the Bayer process of making alumina, and other waste products.

About 75 percent of the reported and estimated 1970 vanadium production shown in figure 76 was derived from iron (titaniferous magnetite) deposits. Output from this source became significant in the 1950's and large in the 1960's, reflecting the inability of the traditional high-grade sources to satisfy the increasing requirements for vanadium. This situation is analogous to that of the copper industry about 50 years ago, when copper requirements exceeded the capacity of the high-grade sources, mainly vein deposits, to meet the demands, and the large-tonnage, low-grade porphyry copper deposits were developed as the principal geologic source of copper.

GEOLOGIC ENVIRONMENT

GEOCHEMISTRY

Vanadium is considered to be a minor element, but it is a rather abundant one. Its crustal abundance is in the order of 100–150 ppm (parts per million), about twice that of copper and zinc and 10 times that of lead. It is one of the lithophile elements that occur mainly in silicate rocks, but it does not form an important part of any common rock-forming mineral. It also has a biophile tendency, so it accumulates in some environments rich in organic materials. Vanadium occurs in three valence states in nature; 3- and 4-valent vanadium are rather insoluble in aqueous solutions, but 5-valent vanadium is relatively soluble.

Geologically, vanadium is a rather well-disciplined element—it has a well-defined geochemical cycle, and it accumulates in only a small number of geologic situations, where its habits and grade range are reasonably consistent.

In igneous rocks, vanadium occurs mainly in the insoluble 3-valent state and substitutes for iron and perhaps aluminum in iron and ferromagnesian minerals. It is most abundant in the mafic igneous rocks (about 200 ppm), less abundant in the ultramafic and intermediate rocks (about 50 ppm), and sparse in the silicic ones (about 25 ppm). Vanadium is concentrated in magmatic magnetite deposits, especially those that are titaniferous, and commonly ranges from 1,000 to 5,000 ppm in these deposits.

Because most of the vanadium in magmas is in the insoluble 3-valent state, not much vanadium is available for hydrothermal transport; hence, only a little (10–100 ppm V) occurs in most hydrothermal ore deposits. However, many titanium-bearing vein deposits and some gold-quartz veins, especially those with gold-telluride minerals, contain some vanadium, commonly about 1,000 ppm.

During weathering of igneous rocks in humid climates, much of the vanadium in the ferromagnesian

minerals apparently goes into the clay minerals that are formed, but it remains in the 3-valent state or oxidizes to the 4-valent state, both of which are relatively insoluble. If erosion is insignificant but chemical leaching is intensive, the residual material may be enriched in vanadium, as are some bauxites and laterites, which commonly contain about 500 ppm V. If, on the other hand, the clay minerals are removed by erosion, most of the vanadium must stay with these clay minerals during transport to places where they accumulate as sedimentary rocks, for argillaceous sediments commonly contain about as much vanadium as do igneous rocks, whereas sandstones contain only about 20 ppm V and limestones about 10 ppm.

During the weathering of igneous, residual, or sedimentary rocks, some vanadium oxidizes to the 5-valent state, especially in the intensive oxidizing conditions of arid climates. In this state the vanadium goes into surface or ground-water solutions and remains in solution over a wide range of acidity and alkalinity. It can be precipitated from solution and locally concentrated in rocks under the following three general conditions:

1. By reaction with hydroxides of aluminum or ferric iron. This process forms or enriches the vanadium concentration in some bauxites and residual or sedimentary iron ores, some of which contain about 500 ppm.

2. By reaction with cations of heavy metals, such as copper, lead, and zinc. This process forms the epigenetic vanadate minerals in the oxidized zones of base-metal deposits. The vanadium concentrations range from a trace to several thousand parts per million V.

3. By reduction in the presence of organic material or biogenetically generated H_2S. If the vanadium-bearing solutions are moving through rocks, epigenetic ore deposits such as those in sandstone in the Colorado Plateau region can be formed. On the other hand, if the vanadium is carried to the seas by surface waters, it can concentrate syngenetically in phosphorites that are rich in organic material, and in carbonaceous shales; some of these shales contain as much as 5,000 ppm V. Furthermore, if the organic materials in these shales are converted to liquid hydrocarbons, the vanadium can be moved as a dissolved constituent; some crude oils contain as much as several hundred parts per million V. Vanadium accumulates in the ashes of these oils, and also in the asphaltic residues resulting from natural or industrial distillation of these oils, and these materials have been used as commercial sources of vanadium.

VANADIUM MINERALS

Fischer and Ohl (1970) listed the names of 110 vanadium minerals, but only some 60 of these are generally accepted by mineralogical authorities; the rest are considered to be inadequately described or unneeded synonyms. Of the accepted vanadium minerals, most are scarce. The important ore minerals are listed below; however, most of the vanadium being produced currently is recovered from ores or materials in which no specific vanadium ore mineral is recognized.

Carnotite: $K_2(UO_2)_2(VO_4)_2 \cdot 3H_2O$. A secondary mineral in surface and near-surface deposits of vanadium and uranium in sandstone; especially common in the Colorado Plateau region.

Coulsonite: $(Fe,V)_3O_4$. A primary mineral exsolved from magnetite in some titaniferous magnetite deposits; also with magnetite in nontitaniferous magnetite deposits in Nevada.

Descloizite-mottramite series: $PbZn(VO_4)OH$-$PbCu(VO_4)OH$. Includes araeoxene, chilëite, cuprodesclozite, dechenite, eusynchite, psittacinite, ramirite, schaffnerite, and vanadite. Secondary minerals in the oxidized parts of base-metal deposits; common in deposits in arid climates.

Montroseite: $(V,Fe)O \cdot OH$. A primary mineral, mostly in deposits in sandstone; common but nowhere abundant.

Patronite: VS_4. A primary mineral in the asphaltite-vein deposit at Mina Ragra, Peru.

Roscoelite: Near $K(V,Al)_3Si_3O_{10}(OH)_2$. A primary mineral, common and abundant in vanadium deposits in sandstone, sparse to moderate in some gold-quartz veins.

Vanadinite: $Pb_5(VO_4)_3Cl$. A secondary mineral in the oxidized parts of some base-metal deposits.

VANADIUM DEPOSITS

DEPOSITS OF MAGMATIC ORIGIN

TITANIFEROUS MAGNETITE DEPOSITS

Vanadium-bearing titaniferous magnetite deposits are associated with mafic and related igneous rocks, most commonly anorthosite and gabbro. These rocks occur in thick stratiform sheets or complex intrusive bodies and are of deep-seated origin; most of those exposed are in continental shield areas and are of Precambrian age; only a few are younger. Magnetite and ilmenite are the principal ore minerals, but some hematite is present in some deposits. These minerals occur in medium- to fine-grained intergrowths and in exsolution and solid-solution relations. Small blebs and exsolution blades of coulsonite have been recognized in magnetite in a few deposits, but no vanadium mineral has been identified in most deposits; almost always, however, vanadium is more abundant in the magnetite (magnetic) concentrates of these deposits than in the ilmenite concentrates. Ore grades in productive deposits vary widely: 16–60 percent Fe, 1.5–38 percent TiO_2, and 0.1–2 percent V_2O_5. Small but varied amounts of chromium, copper, and nickel occur in these deposits; phosphorus is generally sparse.

The ore minerals crystallized with the silicate minerals from the magma, and commonly they occur disseminated in large masses of rock or were segregated by crystal settling into extensive lenses or layers as much as several feet thick. Some bodies of magnetite and ilmenite occur as plugs, dikes, and irregularly shaped masses that presumably were injected into these forms when conditions caused remelting of these minerals in places where they originally crystallized. Deposits vary widely in size —from those too small to be mined to those that consist of several billion tons of ore containing several million tons of vanadium.

NONTITANIFEROUS MAGNETITE DEPOSITS

Nontitaniferous magnetite deposits, by arbitrary definition, contain less than about 1 percent TiO_2. They also generally contain less vanadium but more phosphorus than do the titaniferous magnetite deposits—commonly 0.1 to about 0.5 percent V_2O_5 and more than 0.1 percent P. Their geologic habits are less consistent than those of the titaniferous magnetite deposits; some of them are derived from mafic igneous rocks but others are associated with igneous rocks of intermediate or syenitic composition, and some deposits are apparently wholly magmatic whereas others have the characteristics of contact or hydrothermal replacement bodies. Magnetite, the principal ore mineral in these deposits, occurs in disseminated or massive bodies; the iron content ranges from about 30 to 60 percent Fe. Apatite is present in the deposits rich in phosphorus.

VANADIUM-BEARING HYDROTHERMAL VEIN DEPOSITS

Vanadium is sparse in typical hydrothermal vein deposits except those containing titanium minerals and some containing gold. A few tenths percent V_2O_5 is common in the titanium minerals ilmenite, rutile, and brookite, and also in the uranium-titanium-iron mineral davidite, where these minerals occur in veins. Nolanite ($Fe_3V_{10}O_{23}$, $Fe_3V_8O_{18}$) is intergrown with ilmenite and other vein minerals in the uranium-bearing veins in the Goldfields district, Saskatchewan, Canada (Robinson, 1955). In some gold-quartz veins, especially those containing gold-telluride minerals, roscoelite, the vanadium-bearing mica, is conspicuous. The roscoelite is finely intergrown with quartz and other gangue minerals, and in places it forms small aggregates along the vein walls. The vanadium content of these veins is assumed to be low, although no grade data have been found except for the Kekionga-Magnolia vein, Magnolia district, Colorado, where "a moderate tonnage averaging 2 percent vanadium oxide was blocked out" (Lovering and Goddard, 1950, p. 234).

EPIGENETIC DEPOSITS

VANADATE DEPOSITS

Vanadates of lead, zinc, and copper (vanadinite and minerals of the descloizite-mottramite series) are common in the oxidized zones of base-metal deposits, especially in areas of arid climate and deep oxidation. These minerals form crusts and partly fill cavities in the altered and leached material of the primary base-metal sulfide veins and replacement bodies. The vanadate ore bodies are irregular in shape and varied in size and grade; most are rather small and low in grade. Carbonate rocks are the host to most deposits, but some deposits are in silicic igneous rocks. It is generally assumed that the vanadium was introduced by oxidizing ground waters from remote sources because the vanadium contents of the primary sulfide deposits and the country rocks are virtually nil.

DEPOSITS IN SANDSTONE

Vanadium deposits in sandstone have been the principal source of this metal until recent years; similar but unimportant deposits are known in limestone and shaly sandstone. Typically, the productive deposits occur in stream-laid sandstone lenses several tens of feet thick and 1 mile to several miles wide, interbedded with mudstone of flood-plain or lacustrine origin. These beds accumulated on broad alluvial plains or fans, and all are of late Paleozoic age or younger, probably coincident with the evolutionary development of land plants; coalified fossil plant material is present in most deposits. A few productive deposits are in beds of clean sandstone of eolian origin.

Varied amounts of uranium and copper are associated with vanadium in these deposits. The principal primary ore minerals are silicates and oxides of both vanadium (mainly roscoelite and montroseite) and uranium (coffinite and uraninite) and the common sulfides of copper; carnotite is the principal secondary vanadium-uranium mineral. These minerals chiefly fill the pores of the sandstone, but they also partly replace the sand grains and the plant fossils. Ore grades are commonly 1–2 percent V_2O_5, 0.05–0.25 percent U_3O_8, and a trace to 1 percent Cu. Some ore bodies are irregular in shape, but most of them are tabular; they average only a few feet in thickness and lie nearly parallel to the bedding of the host rock. Ore bodies range in size from a few tons of ore to more than a million tons. Individual deposits are discrete bodies and are separated from neighboring deposits by barren sandstone; nevertheless, deposits tend to be clustered in patches of ground a few miles across and to recur in a favored

stratigraphic zone over broad areas. It is generally assumed that the vanadium and associated metals were introduced by ground waters moving along the sandstone host beds to places where an adequate reducing environment existed; coalified plant material and H_2S generated by bacteria feeding on the plant material likely were the reducing agents.

ASPHALTITE DEPOSITS

The trace amounts of vanadium in crude oils tend to accumulate in the natural asphalts and related materials that are the residues or natural distillation products of crude oils. Many asphaltites contain about 1 percent V_2O_5, and some have yielded samples reported to contain appreciably more vanadium. One asphaltite deposit, that at Mina Ragra, Peru (McKinstry, 1957), has been intensively exploited for vanadium; this deposit was mined from 1907 to 1955 and was the world's principal source of vanadium in the early 1900's. Unoxidized ore in this deposit consisted of quisqueite (a hydrocarbon), coke, and patronite (a vanadium sulfide). Vanadates and vanadium oxide minerals formed the near-surface oxidized ore, some of which was fabulously rich, containing as much as 40 percent V_2O_5. Country rock at Mina Ragra comprises shale and thin-bedded limestone of Cretaceous age. These rocks were invaded by igneous dikes and were cut by numerous faults. The ore minerals and associated material occupy a fracture and permeate the adjoining shale, forming a lens-shaped body, about 50 feet wide and several hundred feet long at the surface, which bottomed at a depth of about 250 feet. The high concentration of vanadium in this deposit may be due to intensive distillation of the original asphaltite and perhaps to a local transfer of vanadium from the country rock by thermal solutions.

DEPOSITS ASSOCIATED WITH ALKALIC IGNEOUS COMPLEXES

The recently developed vanadium deposit at Wilson Springs, Ark., is at the contact of the Potash Sulfur Springs alkalic intrusive complex (Hollingsworth, 1967). The vanadium ore, which contains about 1 percent V_2O_5, occurs as poorly defined bodies in irregular masses of argillic altered rock of both the igneous intrusion and the bordering sedimentary strata. For mining control, ore bodies are delimited by assaying samples; recognizable vanadium minerals are sparse. A similar deposit occurs at the contact of the nearby Magnet Cove alkalic complex (Reed, 1949).

Because of the intensive alteration of the host rocks and deep weathering in the area, the genesis of these deposits is not yet clearly established; ultimately, these deposits may be classified as either contact metasomatic or hydrothermal. But regardless of the mode of concentration, the significant factor in the origin of these deposits may be their association with alkalic igneous complexes. Although this association has not been recognized by most students of the geochemical distribution of vanadium, anomalous amounts of vanadium are reported in analyses of samples from numerous alkalic igneous complexes in various parts of the world. Magnetite and titanium minerals, especially ilmenite, are common in many alkalic intrusives, and vanadium is commonly associated with these minerals in the magmatic stage and to some extent in hydrothermal deposits. If these ideas are correct, alkalic intrusives should be searched more frequently for vanadium deposits. Exploration probably will be difficult, however, for the vanadium probably will not occur in visually recognizable minerals.

RESOURCES

World resources of vanadium in known deposits are very large (Fischer, 1961). They amount to millions of short tons V, representing hundreds of years' supply at the current rate of consumption. Only a few known deposits, however, are rich enough in vanadium to be worked for this metal alone. Most of the vanadium resources are in deposits from which vanadium is being, and will be, recovered as a coproduct or byproduct. Some productive sources contain only trace amounts of vanadium, which is recovered only as a minor byproduct from waste materials.

RESERVES IN PRODUCTIVE DEPOSITS

Significant data on the major and most of the minor sources of vanadium in 1970 are summarized in table 147. This table shows the known reserves in certain deposits, and it also illustrates the diverse geologic materials from which vanadium can be recovered and the ranges in grade of these materials, factors that are important in estimating future production and potential resources in unproductive deposits.

POTENTIAL RESOURCES IN UNPRODUCTIVE DEPOSITS

Large vanadium resources occur in known but unproductive deposits similar to those from which vanadium is being recovered. (In this discussion, "large" implies more than about 1,000,000 short tons V, "moderate" from about 100,000 to 1,000,000 short tons, and "small" less than about 100,000 short tons.) Large resources also occur in carbonaceous shale

TABLE 147.—*Vanadium reserves in the principal sources of vanadium, 1970*

Country and deposit or source	Geologic type of deposit or source	Commodities recovered	V_2O_5 grade (percent)	Reserves [1] Ore (millions of short tons)	Reserves [1] Vanadium (short tons)	Principal source of data [2]
United States:						
Colorado Plateau	Sandstone	U, V	±1.5	5	40,000	Griffith (1970).
Wilson Springs, Ark.	Undetermined	V	1	5	30,000	Do.
Idaho	Phosphate	P, V	.2–.3	(Large)	[3] 45,000	Do.
South-West Africa:						
Otavi district	Vanadate	Cu, Pb, Zn, V	.7	1.6	6,250	South West Africa Co., Ltd., Annual report, 1970.
South Africa:						
Bushveld complex	Titaniferous magnetite.	Fe, V	1.5–2	[4] 212	2,000,000	Nel and Luyt (1964).
Finland:						
Otanmäki	---do	Fe, Ti, V	.47	55	140,000	Marelle (1970).
Norway:						
Rödsand	---do	Fe, Ti, V	.5	11	31,000	Do.
U.S.S.R.:						
Mount Kachkanar [5]	---do	Fe, V	.10–.12	13,500	8,000,000	Sokolov (1970).
Chile:						
El Romeral	Nontitaniferous magnetite.	Fe, V	.3–.4	80	150,000	Alvarado (1970).
Canada:						
Oil refinery	Crude oil	Petroleum products, V	.02	(Large)	?	DeHuff (1965).
France: [6]	Bauxite	Al, V	.1	(Large)	?	Taylor (1971).
Japan:	Ilmenite sands	TiO_2, V	.1–.2	(Large)	?	DeHuff (1971).

[1] Identified deposits from which minerals can be extracted profitably with existing technology and under present economic conditions.
[2] For additional information on the geology and resources of these deposits, see references cited by Fischer and Ohl (1970).
[3] Vanadium estimated by Griffith (1970) that will be recovered from ferrophosphorus slags derived from making elemental phosphorus from Idaho phosphate rock during the 1968–2000 period.
[4] Marelle and Abdulla (1970) reported 200 million metric tons of measured, indicated, and inferred reserves and 1,800 million metric tons of potential ores, totaling 2,200 million short tons of total resources; if the average grade of this material is 1.7 percent V_2O_5, as seems likely, the total vanadium resources amount to about 20,000,000 short tons V.
[5] Some vanadium may have been recovered from the titaniferous magnetite ores at Kusinkoe and Pervouralskoe and perhaps from other iron deposits in the U.S.S.R. in 1970 (Polyakov, 1959).
[6] Some vanadium may also have been recovered from bauxite in other European countries.

beds, from which vanadium has not been recovered commercially. But because many of these unproductive deposits are not developed or even extensively explored, accurate resource appraisals are not possible. Furtermore, many of the known but unproductive deposits are not readily amenable to present metallurgical practices, and most of these deposits would yield vanadium only as a byproduct. For these reasons, it is not possible, except for a few deposits, to predict which ones are most likely to become productive in the foreseeable future.

Titaniferous magnetite deposits in the United States contain large resources of vanadium; those in Alaska (Klemic, 1970; Wells and Thorne, 1953), Wyoming (Dow, 1961), and New York (Balsley, 1943) are the larger and more promising ones. Large resources of the same type occur in Canada (Rose, 1969, 1970), U.S.S.R. (Yudin and Zak, 1971; Sokolov, 1970), Republic of South Africa (see footnote 4, table 147), Australia (Jones, 1965; Daniels, 1967; Hockley, 1971), and perhaps mainland China (Nishiwaki, 1970; Hsing, 1959). Of the unproductive titaniferous magnetite deposits, those in the Singhbhum area, Bihar and Orissa, India, seem to be the most favorable to yield vanadium as the principal product; ore reserves total about 20,000,000 tons and perhaps average about 2 percent V_2O_5 (Roy, 1969). Vanadium might be recoverable from the deposits at Lake Sanford, N.Y., and Allard Lake and St. Urbain, Quebec, Canada, that are being mined for titanium.

Nontitaniferous magnetite deposits being mined for iron ore at Buena Vista Hills, Nev. (Reeves and Kral, 1955; Radtke, 1962), and the Savage River area, Tasmania, Australia (Evoy, 1970), contain about 0.3–0.5 percent V_2O_5, about that in the deposit at El Romeral, Chile (table 147), from which vanadium is being recovered. Vanadium resources in the deposits at Buena Vista Hills and Savage River are moderate. Although the vanadium content of the nontitaniferous magnetite deposits in the Kiruna and Gällivare districts, Sweden, is only 0.1–0.2 percent V_2O_5, these deposits contain a large resource of vanadium.

During World War II, Germany recovered considerable vanadium from sedimentary iron ores in northwestern Europe that contain only 0.02–0.2 percent V_2O_5 (Fischer, 1946). Although vanadium recovery from these ores presumably is not economically feasible under present conditions, the wartime operations show that recovery is technologically possible; hence, these deposits and similar ones qualify as a vanadium resource. The reserves of the

minette-type iron ores of northern France, Western Germany, and central England are large (Marelle, 1970), and probably each area contains a moderate to large resource of vanadium. Three similar deposits in the U.S.S.R.—Ayatskoe (0.1 percent V_2O_5), Lisakovskoe (0.1 percent V_2O_5), and Kerch (0.05 percent V_2O_5) (Sokolov, 1970; Bardin, 1957)—each contain large iron-ore reserves (Sokolov, 1970) and moderate to large vanadium resources. Although vanadium probably is not being recovered from these ores, Slotvinskii-Sidak and Liakishev (1970, p. 202) stated: "Large vanadium reserves are concentrated in the iron ores of Lisakovskoe, Kerchinskoe, Ayatskoe, and other deposits. Thus, in projected amount of recovery of ores of the Lisakovskoe deposit, some tens of thousands of tons of vanadium pentoxide will be recovered in the iron concentrate (with 48–50 percent Fe and 0.15–0.25 percent V_2O_5)."

Magnetite and ilmenite sands commonly contain 0.1–0.5 percent V_2O_5; those rich in magnetite, especially those derived from titaniferous magnetite deposits, are the ones generally richer in vanadium. Some of these sand deposits occur along streams, but most of them are on beaches. They occur in many parts of the world, and some of them contain large reserves of the black minerals and small to moderate resources of vanadium. Japan is recovering some vanadium from waste sulfuric acid derived from producing titanium dioxide from ilmenite sands (DeHuff, 1971). During World War II Japan recovered vanadium and titanium from magnetite-rich beach sand utilized principally as a source of iron. Perhaps the sand deposits that offer the greatest potential for vanadium production are those in New Zealand that are now being exploited for iron (Ridley, 1968). These deposits contain several hundred million tons of sand, the concentrates of which contain 53–60 percent Fe, 8–10 percent TiO_2, and 0.3–0.5 percent V_2O_5 (Fyfe, 1952).

Potential resources of vanadium in undiscovered deposits in sandstone in the Colorado Plateau region, United States, are probably small; likely they do not much exceed known reserves (table 147). Similar deposits of vanadium with uranium in sandstone are known in other parts of the United States and in some foreign countries, notably the U.S.S.R., Gabon, Argentina, and Australia, but generally these deposits have a lower vanadium content than the vanadium-rich deposits of the Colorado Plateau, and therefore they do not seem to offer a significant vanadium potential.

Occurrences of vanadate minerals are widespread, especially in arid parts of the world, but accumulations of these minerals in amounts necessary for mining are few; resources are judged to be negligible compared to other geologic types of vanadium deposits.

Many crude oils contain little or no vanadium, but some, especially the asphalt-base oils, contain up to several hundred parts per million V (Whisman and Cotton, 1971). Although it would hardly be conventional to classify an oil pool as a vanadium deposit, industrial and natural residues of petroleum are, nevertheless, commercial sources of vanadium and they might become more significant sources in the future. Vanadium is recovered from the ash and soot of oil-burning furnaces and from refinery residues; pollution-control practices may enhance the chance of recovery from these sources in the future. The recovery of vanadium from the residue of refining Athabaska tar sand, Alberta, Canada, has been proposed (Oil and Gas Journal, 1967); although these sands contain only about 240 ppm V, the quantity of material being processed could yield annually about a quarter of the current North American vanadium requirements. Similar deposits, if exploited for petroleum products, could also be sources of vanadium. The vanadium-bearing asphaltite deposit at Mina Ragra, Peru, was the richest vanadium deposit known, and it had yielded about one-fourth of the world's total vanadium output by the time it was mined out in 1955. No other sizable asphaltite deposit of comparable grade is known, but many deposits containing about 1 percent V_2O_5 have been reported, especially in Peru (Larson and Welker, 1947) and Argentina (Wright, 1940).

Certain carbonaceous shales, oil shales, phosphatic shales, and graphitic schists contain 0.2 to nearly 1 percent V_2O_5; higher grade samples are also reported. Some of the vanadium-bearing shale deposits are tens of feet thick and cover broad areas —obviously these deposits contain enormous tonnages of rock and represent large resources of vanadium. References to many carbonaceous shale deposits are given by Tourtelot (1970) and by Fischer and Ohl (1970). Notable examples of these shales occur in Idaho and adjoining States (Fischer, 1961), in Kazakhstan, U.S.S.R. (Ankinovich, 1961), in the high Andes of Peru (Larson and Welker, 1947), and in Queensland, Australia (Taylor, 1971).

PROSPECTING TECHNIQUES

The basic tools for prospecting for vanadium are a knowledge of the geologic types of deposits in which vanadium is apt to occur and a knowledge of the geologic habits and mineral associations of such deposits. The vanadium ore minerals in the vana-

date deposits and in the deposits in sandstone are visually recognizable in the field, and of course the presence of associated uranium in the sandstone deposits is readily detected by its radioactivity. The presence of vanadium in iron deposits much be determined by analysis, even though the principal ore minerals in these deposits can be recognized visually. Analyses are also generally needed to detect the presence of vanadium in phosphate rock, carbonaceous shale, and asphaltite, although in places recognizable vanadium minerals develop on the weathered outcrops of these deposits. Generally, vanadium is not amenable to geochemical exploration techniques of sampling soils and stream sediments, as are the base metals and some other metals, because vanadium is not so readily soluble and because it has a high background content in many types of rocks.

PROBLEMS FOR RESEARCH

The demand for vanadium is expected to increase appreciably. World resources of vanadium are very large, but most of the raw materials containing these resources will yield vanadium only as a byproduct, commonly a minor one, and so output of vanadium is largely dependent on the requirements for other commodities and on technological practices that permit the recovery of small amounts of vanadium.

Domestic requirements for vanadium are expected to exceed domestic output. In order to avoid dependence on foreign supplies, new vanadium deposits must be found or the means must be developed to recover byproduct vanadium profitably from known sources. Potentially recoverable vanadium is currently being lost from some operations that mine magnetite and phosphate rock and some that refine or burn crude oil.

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ZEOLITES IN SEDIMENTARY ROCKS

By Richard A. Sheppard

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ABSTRACT OF CONCLUSIONS

Zeolites are among the most common authigenic silicate minerals in sedimentary rocks; they occur in rocks that are diverse in age, lithology, and depositional environment. Zeolites are particularly common in Cenozoic sedimentary rocks that originally contained abundant silicic vitric material. Most zeolites in sedimentary rocks formed during diagenesis by the reaction of volcanic glass with interstitial water which originated as either meteoric water or connate water of a saline, alkaline lake. Although about 20 different zeolites have been reported from sedimentary rocks, only analcime, chabazite, clinoptilolite, erionite, ferrierite, heulandite, laumontite, mordenite, and phillipsite commonly make up the major part of zeolitic rocks. Nearly monomineralic beds of zeolites are known, but most zeolite rocks also contain clay minerals, silica minerals, and feldspars of authigenic origin.

Production of natural zeolites in the United States is currently only several hundred tons per year. The abundance and variety of zeolite deposits in the United States, the unique properties of the zeolites, and the seemingly low cost of mining suggest potential uses in many industrial and agricultural processes. Chemical and structural modifications of the natural materials could further increase their potential. When new markets for zeolites are developed, the United States will not only be self-sufficient but will probably become a major exporter.

The total of identified, hypothetical, and speculative resources of zeolites in the United States is conservatively estimated at more than 10 trillion tons. Total resources of zeolites in the rest of the world have not yet really begun to to be cataloged.

INTRODUCTION

Zeolites—crystalline hydrated aluminosilicates of the alkalis and alkaline earths—are important rock-forming constituents in sedimentary rocks and are potentially valuable industrial minerals. They have a framework structure that encloses interconnected cavities occupied by the relatively large cations and water molecules. The cations, chiefly sodium, potassium, and calcium, and the water have considerable freedom of movement within the structure and give the zeolite their cation-exchange and reversible-dehydration properties. Some zeolites have essential contents of barium, strontium, or magnesium. The basic structure of all zeolites consists of $(Si,Al)O_4$ tetrahedra wherein each oxygen is shared between two tetrahedra; thus, the atomic ratio $O:(Si+Al)$ is 2. The net negative charge of the structure is balanced by the cations. The porous framework of the zeolites enables them to act as molecular sieves for the separation of molecular mixtures according to the size and shape of the molecular compounds.

More than 30 distinct species of zeolites occur in nature. Numerous zeolites have also been synthesized, but many of these have no natural counterparts. Most zeolites have a specific gravity of 2.0–2.3 and indices of refraction of 1.44–1.52. Zeolites rich in barium or strontium commonly have higher specific gravities and indices of refraction. Because the zeolites have similar physical properties, X-ray diffraction techniques are generally used for identification.

Synthetic zeolites have been produced commercially in the United States since the early 1950's. These synthetic zeolites are used principally as catalysts, selective sorbents, and desiccants; they are

now utilized in about 90 percent of the petroleum catalytic cracking installations and have greatly increased the recovery of gasoline. Natural zeolites, however, have found only limited use in this country. Clinoptilolite is used to remove cesium from radioactive wastes (Brown, 1962), and chabazite is used to desiccate mildly acidic natural gas. Zeolitic tuff has been used as a pozzolan in cement.

In Japan, on the other hand, zeolites have been extensively mined and utilized since their discovery there in sedimentary deposits in 1949. Clinoptilolite and mordenite are the only zeolites currently mined in Japan, and they are utilized chiefly in the fields of agriculture and animal husbandry. Minato and Utada (1969) described the following uses: Desiccant for gases, separator of oxygen from air, adsorbent for obnoxious odors in farm yards, filler and whitening agent for paper, and a soil conditioner to increase the effectiveness of chemical fertilizers. More clinoptilolite is mined in Japan for the last use listed than for any of the others.

Some of the natural zeolites may find applications in pollution control. For example, laboratory and pilot-plant studies by Pacific Northwest Laboratory, Battelle Memorial Institute, Richland, Wash. (Mercer and others, 1970), indicate that clinoptilolite is effective in the removal of ammonia from wastewater. Also, recent studies suggest that mordenite may be suitable for the removal of SO_2 from stack gases.

The United States is self-sufficient with respect to the present fledgling zeolite industry. Because of the large potential zeolite resources and the diverse zeolite mineralogy, the United States will not only remain self-sufficient when new markets develop but will probably become a major exporter.

EXPLOITATION

Production figures have not been published for natural zeolites in the United States; however, small tonnages were mined from upper Cenozoic tuffs. Several hundred tons of chabazite, clinoptilolite, and erionite have been mined each year since the mid-1960's; the mined deposits are near Bowie, Ariz., near Hector, Calif., and in Jersey Valley, Nev., respectively.

Exploration and sampling of bedded zeolite deposits by commercial organizations have been active since the late 1950's in Arizona, California, Nevada, Oregon, Texas, and Wyoming. The exploration peaked in the early 1960's, when the search concentrated on natural molecular-sieve zeolites that might compete with the synthetic zeolites. Since 1970, exploration has accelerated again. This time the emphasis is on the location of zeolite deposits suitable for pollution-control processes.

Japan is probably the world's leading producer of natural zeolites. Since the mid-1960's, Japan has had an annual production of about 100,000 tons. About half of this production is from one mine, at Itaya, Honshu. Clinoptilolite and mordenite are the only zeolites currently mined in Japan.

GEOLOGIC ENVIRONMENT

Zeolites have been known since the mid-1750's, and they occur in rocks that are diverse in age, lithology, and geologic setting. Zeolites have been recognized in sedimentary deposits since 1891, when Murray and Renard (1891) described phillipsite in deep-sea deposits. Prior to the early 1950's, however, most zeolite occurrences were reported from fractured fillings and vesicle fillings in igneous rocks, particularly in basaltic rocks. Most of the large attractive zeolite specimens in museum collections were obtained from igneous rocks. In recent years, zeolites have been recognized as important rock-forming constituents in low-grade metamorphic rocks and in a variety of sedimentary rocks (Hay, 1966). The zeolites in sedimentary rocks are very finely crystalline and do not appeal to mineral collectors; however, deposits of this type are voluminous and have great economic potential. The remainder of this chapter summarizes those zeolite resources in sedimentary deposits.

Of the more than 400 published reports that describe zeolites in sedimentary rocks throughout the world, more than 75 percent were published in the last dozen years. The factors chiefly responsible for this recent surge of reports are (1) the widespread use of X-ray powder diffraction techniques in the study of fine-grained sedimentary rocks, (2) the exploration for zeolite deposits suitable for commercial use, and (3) the early review papers by Coombs, Ellis, Fyfe, and Taylor (1959) and Deffeyes (1959), both of which emphasized the widespread and relatively common occurrences of diagenetic or authigenic zeolites in sedimentary rocks.

Zeolites are among the most common authigenic silicate minerals that occur in sedimentary rocks, and they have formed in sedimentary rocks of diverse lithology, age, and depositional environment. Those zeolites given in table 148 have been reported from sedimentary rocks; however, some, such as faujasite, gismondine, gonnardite, scolecite, and thomsonite, generally occur in trace amounts and are rarely reported. Only nine zeolites commonly make up the major part of zeolitic rocks. These are analcime, chabazite, clinoptilolite, erionite, ferrierite,

TABLE 148.—*Zeolites reported from sedimentary rocks*

Zeolite	Formula
Analcime	$NaAlSi_2O_6 \cdot H_2O$
Chabazite	$(Ca,Na_2)Al_2Si_4O_{12} \cdot 6H_2O$
Clinoptilolite	$(Na_2,K_2,Ca)_3Al_6Si_{30}O_{72} \cdot 24H_2O$
Epistilbite	$(Ca,Na_2)_3Al_6Si_{18}O_{48} \cdot 16H_2O$
Erionite	$(Na_2,K_2,Ca)_{4.5}Al_9Si_{27}O_{72} \cdot 27H_2O$
Faujasite	$(Na_2,Ca)_{1.75}Al_{3.5}Si_{8.5}O_{24} \cdot 16H_2O$
Ferrierite	$(K,Na)_2(Mg,Ca)_2Al_6Si_{30}O_{72} \cdot 18H_2O$
Gismondine	$(Ca,Na_2,K_2)_4Al_8Si_8O_{32} \cdot 16H_2O$
Gonnardite	$Na_2CaAl_4Si_6O_{20} \cdot 5H_2O$
Harmotome	$(Ba,Na_2)_2Al_4Si_{12}O_{32} \cdot 12H_2O$
Heulandite	$(Ca,Na_2)_4Al_8Si_{28}O_{72} \cdot 24H_2O$
Laumontite	$Ca_4Al_8Si_{16}O_{48} \cdot 16H_2O$
Mordenite	$(Na_2,K_2,Ca)Al_2Si_{10}O_{24} \cdot 7H_2O$
Natrolite	$Na_4Al_4Si_6O_{20} \cdot 4H_2O$
Phillipsite	$(K_2,Na_2,Ca)_2Al_4Si_{12}O_{32} \cdot 12H_2O$
Scolecite	$Ca_2Al_4Si_6O_{20} \cdot 6H_2O$
Stilbite	$(Ca,Na_2)_4Al_8Si_{28}O_{72} \cdot 28H_2O$
Thomsonite	$NaCa_2Al_5Si_5O_{20} \cdot 6H_2O$
Wairakite	$CaAl_2Si_4O_{12} \cdot 2H_2O$
Yugawaralite	$CaAl_2Si_6O_{16} \cdot 4H_2O$

heulandite, laumontite, mordenite, and phillipsite. Analcime and clinoptilolite are by far the most abundant zeolites in the sedimentary rocks. All nine of these common zeolites in sedimentary rocks show a considerable range in Si:Al ratios and cation contents. Except for heulandite and laumontite, they are generally alkalic and more siliceous than their counterparts that occur in mafic igneous rocks. Summaries of their chemistry are given by Deer, Howie, and Zussman (1963), Hay (1966), Sheppard (1971), and Utada (1970).

Most zeolites in sedimentary deposits formed after burial of the enclosing sediments by the reaction of aluminosilicate materials with the pore water. Silicic volcanic glass is the aluminosilicate material that most commonly served as a precursor for the zeolites, although materials such as clay minerals, feldspars, feldspathoids, nad gels also have reacted locally to form zeolites. Hay (1966) showed that authigenic zeolites and associated silicate minerals can be correlated with the following factors: (1) composition, grain size, permeability, and age of the host rocks, (2) composition of the pore water including pH, salinity, and proportion of dissolved ions, and (3) depth of burial of the host rock. Except for laumontite and possibly some heulandite, the common zeolites generally occur in tuffaceous sedimentary rocks that have not been deeply buried or exposed to hydrothermal solutions.

Classification of the diverse zeolitic sedimentary rocks is difficult, but the following tenuous classification is based on geologic setting and is offered as a basis for further discussion: (1) hydrothermal, (2) burial metamorphic, (3) weathering, (4) open system, and (5) closed system. The hydrothermal type includes those zeolites associated with metallic deposits such as those at the East Tintic district, Utah (Lovering and Shepard, 1960), and especially with hot-spring deposits. Well-known examples of the latter are at Yellowstone National Park, Wyo. (Fenner, 1936; Honda and Muffler, 1970), Wairakei, New Zealand (Steiner, 1953, 1955), and Onikobe, Japan (Seki and others, 1969). Zeolites of geothermal areas commonly show a vertical zonation, and the downward succession of mineral assemblages seems to correlate with an increase in temperature. At Wairakei and Onikobe, for example, the downward succession is characterized by mordenite, laumontite, and then wairakite.

Zeolites of the burial metamorphic type were originally recognized by Coombs (1954) in Triassic sedimentary rocks of the Southland syncline, New Zealand. Coombs, Ellis, Fyfe, and Taylor (1959) demonstrated a vertical zonation of mineral assemblages that is characterized by a downward succession of clinoptilolite-heulandite-analcime, laumontite-albite, and then prehnite-pumpellyite-albite. Rocks rich in prehnite and pumpellyite commonly grade downward into rocks typical of the greenschist metamorphic facies. Locally, a zone rich in wairakite occurs between the laumontite-albite and prehnite-pumpellyite-albite zones or overlaps these zones. The zeolites and associated silicate minerals of the burial metamorphic type commonly occur in marine volcaniclastic strata that are more than 10,000 feet thick and locally are as much as 40,000 feet thick. The vertical succession of mineral assemblages is one of decreasing hydration with depth and is generally thought to be temperature dependent; however, chemical variables may prove to be equally important. Besides occurrences in New Zealand, zeolitic rocks of the burial metamorphic type have been recognized in Australia (Packham and Crook, 1960), Puerto Rico (Otálora, 1964), U.S.S.R. (Kossovskaya and Shutov, 1963), Japan (Seki, 1969; Utada, 1970), British Columbia, Canada (Surdam, 1968), and the United States. Laumontite-bearing rocks of the burial metamorphic type occur in central Oregon (Dickinson, 1962; Brown and Thayer, 1963), in Mount Rainier National Park, Wash. (Fiske and others, 1963), and near Cache Creek, Calif. (Dickinson and others, 1969).

Zeolites of the weathering type are volumetrically rather minor, but many deposits have probably been overlooked. Analcime was recently reported from alkaline, saline soils of the eastern San Joaquin Valley, Cailf. (Baldar and Whittig, 1968). The analcime was detected to a depth of about 4 feet, and its abundance decreased with depth. Hay (1963a) recognized analcime, chabazite, natrolite, and phil-

lipsite in alkaline, saline soil profiles at Olduvai Gorge, Tanzania. Surface concentrations of analcime were also reported in reddish, root-marked claystones on the Luboi Plain, Kenya (Hay, 1970).

The most voluminous and potentially valuable zeolite deposits belong to the open- and closed-system types. The terms, "open system" and "closed system," are used in a hydrologic sense rather than in a thermodynamic sense. Deposits of the open-system type formed by the reaction of volcanic glass with subsurface water that originated as meteoric water. The original volcanic material commonly was deposited in marine or fluviatile environments or was air laid on the land surface. Deposits of the closed-system type formed by the reaction of volcanic glass with the connate water trapped during sedimentation in a saline, alkaline lake.

Deposits of the open-system type commonly formed in thick tuffaceous strata and show a vertical zonation of authigenic silicate minerals. Hay (1963b) proposed hydrolysis and solution of silicic glass by subsurface water to account for the formation of clinoptilolite in tuff and tuffaceous claystone in the lower part of the Tertiary John Day Formation in central Oregon. The upper part of the formation contains unaltered glass or montmorillonite. The authigenic mineral zonation is more complex in the Tertiary tuffs at the Nevada Test Site (Hoover, 1968). An upper zone consists of unaltered glass with local concentrations of chabazite and clay minerals. Zeolitic tuff continues downward for as much as 6,000 feet and is characterized by a downward succession of zones rich in clinoptilolite, mordenite, and then analcime. The zeolite zones of the open-system type commonly cut across stratigraphic boundaries.

Zeolite deposits of the closed-system type formed during diagenesis in alkaline, saline lakes, commonly of the sodium carbonate-bicarbonate variety. Brine of this composition generally has a pH greater than 9, which probably accounts for the relatively rapid solution of vitric material and precipitation of zeolites. The authigenic silicate mineralogy can be correlated with the salinity in deposits of the closed-system type. The Pleistocene deposits of Lake Tecopa, Calif. (Sheppard and Gude, 1968), are characteristic of the closed-system type. Vitric material is unaltered or partly altered to clay minerals in tuff deposited in fresh water near the lake shore and inlets; however, the tuffs consist of zeolites where deposited in moderately saline water and of potassium feldspar where deposited in the highly saline and alkaline water of the central part of the basin. Thus, individual tuffs show a lateral zonation in a basinward direction of unaltered glass to zeolites and then to potassium feldspar. Zeolitic tuffs at Lake Tecopa consist chiefly of phillipsite, clinoptilolite, and erionite. Chabazite is a minor constituent of tuffs at Lake Tecopa, but it is locally the major constituent in zeolitic tuffs of other saline lacustrine deposits. In some deposits of the closed-system type, such as the Miocene Barstow Formation of California (Sheppard and Gude, 1969) and the Eocene Green River Formation of Wyoming (Surdam and Parker, 1972) a zone of analcime separates the other zeolites from the zone of potassium feldspar. In addition to clay minerals, zeolites, and potassium feldspar, deposits of the closed-system type locally contain opal or chalcedony, searlesite ($NaBSi_2O_6 \cdot H_2O$), fluorite (CaF_2), or dawsonite ($NaAl(CO_3)(OH)_2$) of authigenic origin.

PROSPECTING TECHNIQUES

Prospecting for bedded zeolite deposits is difficult because the zeolites are finely crystalline and resemble bedded diatomite, feldspar, or bentonite in the field. Zeolitic tuffs generally have an earthy luster and are resistant. Although some zeolitic tuffs are pastel shades of yellow, brown, red, or green, many are white or pale gray. If the zeolitic tuff is nearly monomineralic, certain gross physical properties of the rock may aid field recognition (Sheppard and Gude, 1969, p. 17–18). Utilizing the ion-exchange and molecular-sieve properties of zeolites, Helfferich (1964) designed a "field" test for the recognition of zeolites. Helfferich's test distinguishes zeolites from clay minerals, feldspars, and volcanic glass, but the test will not identify the zeolite species. My experience with Helfferich's test suggests that it is better suited to the laboratory than to the field.

X-ray powder diffraction analysis of bulk samples is the technique generally used for identification of the zeolites in sedimentary rocks. This method also permits a semiquantitative estimate of the abundance of zeolites and associated minerals in the samples. Tuffaceous strata are sampled, and then the samples are brought to the laboratory for examination by X-ray diffraction. Fresh tuff is generally distinguishable from altered tuff in the field, so only the altered parts of the tuffaceous rocks are sampled in both vertical and lateral directions. Once zeolites have been identified by X-ray diffraction, an additional detailed sampling is necessary to ascertain the distribution and abundance of the zeolites and associated authigenic minerals. Inasmuch as the samples must be returned to the laboratory for X-ray study, the availability of a truck-mounted X-ray diffractometer unit, suitable for field use, would

facilitate the location of favorable targets and provide a guide for a meaningful sampling program.

POTENTIAL RESOURCES

Evaluation of zeolite resources is hampered by the paucity of data on the extent and grade of the identified deposits. Although more than 100 occurrences of zeolites in sedimentary rocks of the United States have been recorded (Sheppard, 1971), information such as the grade, mineralogy, and vertical and lateral extent of the zeolitic rock and the thickness of overburden are lacking except for several deposits. The occurrence of zeolites in a certain sedimentary unit is commonly recognized from the examination of only one sample. Nevertheless, very large tonnages of zeolitic tuff of high purity are known from the Cenozoic deposits of the Western United States and the Gulf Coastal Plain.

The only published estimate of zeolite resources in the United States was made by Deffeyes (1968), who estimated that about 120 million tons of clinoptilolite, chabazite, erionite, mordenite, and phillipsite occur in near-surface deposits of the Basin and Range province. This estimate is probably conservative for the zeolite deposits of the Basin and Range province, and the potential zeolite resources of the United States is probably several orders of magnitude greater. If the restraints of grade and depth of overburden are ignored, the total of identified, hypothetical, and speculative zeolite resources in the United States is conservatively estimated at 10 trillion tons. The nine common zeolites listed in approximate order of decreasing abundance are clinoptilolite (including heulandite), analcime, mordenite, erionite, phillipsite, chabazite, laumontite, and ferrierite. The United States probably has the world's largest potential resources of high-grade chabazite, erionite, and phillipsite. The only high-grade deposits of ferrierite in the world have been reported from central Nevada (Regis, 1970).

If an estimate of zeolite resources in the United States is difficult to make, a meaningful estimate of zeolite resources for the other countries of the world is impossible to make. Zeolites have been reported in sedimentary rocks from many other countries, and their occurrences were summarized by Hay (1966) and Iijima and Utada (1966). However, no resource estimates have been published. In addition to the foreign zeolite deposits mentioned in these summaries and those foreign deposits mentioned previously in this chapter, apparently extensive and relatively high grade zeolite deposits occur in France (Estéoule and others, 1971), Germany (F. A. Mumpton, written commun., 1972), Italy (Sersale, 1960; Alietti and Ferrarese, 1967; Alietti, 1970), Yugoslavia (Stojanović, 1968), Hungary (Nemecz and Varju, 1962), and Bulgaria (Alexiev, 1968). Most of the occurrences are in Cenozoic tuffaceous rocks, and the major zeolite is clinoptilolite.

Additional deposits of zeolites will undoubtedly be discovered in the Western United States and in other countries of the world. Zeolites can form from a variety of aluminosilicate materials during diagenesis, providing the interstitial water has a relatively high pH and high concentration of alkalis. The purest zeolite deposits, however, form from volcanic ash that lacks crystal and rock fragments. In the Western Hemisphere, zeolites have not been reported from countries south of the United States except Argentina. An examination of upper Mesozoic and Cenozoic tuffaceous rocks will probably reveal large zeolite deposits in Mexico and many of the countries of Central America and western South America. Future exploration will also probably identify bedded zeolite deposits in the volcanic terranes of southern Europe, eastern Africa, and southern Asia.

RESEARCH NEEDED

The genesis of zeolites in sedimentary rocks is understood in general terms; however, several problems merit additional study. Phillipsite and clinoptilolite are the chief zeolites in young deep-sea deposits, but the relative importance of the precursor materials and the interstitial fluids in their formation is unknown. Tuffs of originally rhyolitic composition in deposits of alkaline, saline lakes characteristically contain a variety of zeolite minerals, but the factors that control which particular zeolite forms are poorly understood. Low-temperature experimental studies combined with studies of the zeolites and associated interstitial fluids in Holocene tuffs presently undergoing alteration may provide some answers. Another problem that warrants investigation is the relationship of the chemistry of a certain zeolite species to the geologic setting of the host rock.

Other research of a technological nature that deserves consideration is (1) development of techniques for the separation of zeolites from the gangue, (2) development of techniques for the separation of one zeolite from another, and (3) chemical or structural modifications of natural zeolites to increase their usefulness. Natural zeolites or zeolitic rocks will undoubtedly be used in many industrial and agricultural processes; however, additional applied research is necessary to achieve these goals.

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ZINC

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ABSTRACT OF CONCLUSIONS

Zinc, a ubiquitous minor element in the earth's crust, has been used industrially for many centuries, at first only as an alloy component, later as the metal and as a component of chemical compounds. Today it stands, in tonnage produced, as the fourth most important metal in world trade. About 150 million metric tons has been used since the beginning of the 19th century, and projected growth rates suggest that this amount will more than double by the end of the 20th century. Current annual world production exceeds 5 million metric tons. Of this tonnage the United States produces about 9 percent, but it consumes more than three times the amount it produces. World resource estimates indicate that recoverable identified resources (that is, reserves) are about 235 million metric tons, of which 45 million is in the United States. Total world identified and undiscovered zinc resources are estimated at over 5 billion metric tons, about one-tenth of which is in ores of grade sufficient to be exploitable under existing economic conditions. Zinc is produced from mines in more than 40 countries on all continents except Antarctica: six leading countries— Canada, Russia, United States, Peru, Mexico, and Australia—produce more than 60 percent of the world's total.

The resource potential of zinc suggests that several hundred million tons of contained metal are in conventional deposits that await discovery by conventional search techniques and improvement of recovery methods; these conventional resources are dominated by the massive sulfide ores in metamorphic rocks, in which zinc occurs chiefly with copper and lead, and by the stratabound deposits in carbonate rocks, in which lead is an essential coproduct and cadmium a significant byproduct. Potential resources in both conventional and unusual deposits are estimated in the billions of tons; these include both low-grade and higher grade deposits for which new recovery methods must be developed before they can be exploited, such as the Kupferschiefer in Europe, the base metal-rich muds deposited from hot brines in Red Sea deeps, and the lead- and zinc-bearing manganese nodules on the Pacific sea floor. The concept that zinc can be concentrated in the geochemical environments of tropical and per-

haps semitropical laterites, both modern and ancient, offers considerable promise for the discovery of significant high-grade tonnages of shallow nonsulfide ores that can be worked by large-scale open-pit methods. Such ores are of interest also because they do not contribute to sulfur emission problems during reduction.

INTRODUCTION

Zinc is necessary to modern living and, in tonnage produced, stands fourth among all metals in world production—being exceeded only by iron, aluminum, and copper. Elemental zinc is a bluish-white metal when freshly cast and has a specific gravity of 7.13. Its melting and boiling points are 419°C and 906°C, respectively. It alloys readily with other metals and is chemically active as well. On exposure to air it develops a thin protective impervious gray oxide film, an important characteristic in its use. Most commercial zinc is produced in the metallic form called slab zinc and comes from the smelter in various sizes and shapes. Some zinc concentrates are converted directly to zinc oxide for use as such. Primary slab zinc is prepared in several grades depending on impurities, ranging from Prime Western with a minimum zinc content of 98.0 percent to Special High Grade with a minimum zinc content of 99.99 percent. The impurities are chiefly lead, iron, and cadmium; trace quantities of copper, tin, and aluminum may also be present.

Zinc is utilized chiefly in the automobile, household appliance, and hardware industries. The metal has three major uses: (1) for zinc-base alloy die castings, (2) for galvanizing iron and steel products, and (3) in the manufacture of the copper-zinc alloy, brass. In the United States, these three uses account for about 90 percent of the total consumption. Other important uses are as rolled zinc metal and in the preparation of zinc compounds for the manufacture of a variety of industrial products—for example, zinc oxide in rubber and in paints. (See tables 149–151.) Possible substitutes for zinc in die casting are magnesium and aluminum, particularly if a weight limitation is important. Plastics are also competing in the die-casting field as metal-on-plastic plating techniques are being perfected. Aluminum is being substituted for galvanized sheet steel in the light-construction industry, but there appears to be no satisfactory alternate to zinc for the large tonnages used for the corrosion protection of the wide variety of iron and steel products needed by modern civilization. Heindl (1970) gave additional information on the uses of zinc and its place in industry.

TABLE 149.—*Consumption of zinc, in short tons, in the United States, 1969*

Slab zinc	1,368,323
Ores (recoverable zinc content)	126,712
Secondary (recoverable zinc content)[1]	302,075
Total	1,797,110

[1] Excludes redistilled slab and remelt zinc. From Moulds, (1969, p. 1159, table 15).

TABLE 150.—*Slab zinc consumption, in short tons, in the United States, by industry uses*

[NA, not available]

Industry and product	1965	1969
Galvanizing:		
Sheet and strip	270,826	251,625
Wire and wire rope	43,884	32,348
Tubes and pipes	63,224	65,898
Fittings (for tubes and pipes)	8,641	11,418
Tanks and containers	NA	5,561
Structural shapes	NA	19,454
Fasteners	NA	5,536
Pole-line hardware	NA	9,409
Fencing, wire cloth, and netting	NA	17,984
Job galvanizing	51,011	NA
Other and unspecified uses	44,835	57,091
Total	482,421	476,324
Brass products:		
Sheet, strip, and plate	58,864	90,777
Rod and wire	45,510	56,989
Tube	10,030	10,928
Castings and billets	3,050	5,958
Copper-base ingots	7,402	13,642
Other copper-base products	1,992	1,175
Total	126,848	179,469
Zinc-base alloy:		
Diecasting alloy	629,809	565,839
Dies and rod alloy	535	504
Slush and sand casting alloy	7,626	10,048
Total	637,970	576,391
Rolled zinc	45,882	48,650
Zinc oxide	25,781	41,447
Other uses:		
Wet batteries	1,188	1,536
Desilverizing lead	2,444	3,957
Light-metal alloys	8,124	7,562
Other[1]	23,434	32,987
Total	35,190	46,042
Grand total	1,354,092	1,368,323

[1] Includes zinc used in making zinc dust, bronze powder, alloys, chemicals, castings, and miscellaneous uses not elsewhere mentioned. From Moulds (1969, p. 1160, table 16).

TABLE 151.—*Distribution of zinc oxide and leaded zinc oxide shipments, in short tons, by industries*

[W, withheld to avoid disclosing individual company confidential data; included with "Other." Data from Moulds (1969, p. 1162, table 22)]

Industry	1965	1969
Zinc oxide:		
Rubber	103,057	115,988
Paints	30,249	25,170
Ceramics	10,009	9,469
Chemicals	11,365	22,775
Agriculture	977	4,007
Photocopying	W	27,566
Floor covering	363	W
Other	30,550	14,748
Total	186,570	219,723
Leaded zinc oxide:		
Paints	10,951	4,905
Rubber	899	2,051
Other and unspecified		
Total	11,850	6,956

EXPLOITATION

The zinc industry of modern times began with the smelting of the metal at Liege, Belgium, in 1806. Historically, however, zinc was an alloy constituent long before it was used in its purer metallic form. Brass was known to the Greeks and Romans, probably from about the 2d century before the Christian era, and was produced by melting copper with zinc minerals. The identity of zinc as a distinct metal was not known in the western world until the Middle Ages when it began to be imported from China and India. Ensuing centuries saw increasing amounts imported by Europeans until finally the technology itself was brought from China to England in about 1730.

Belgium and Germany were the chief zinc-producing countries during the 19th century and produced about 70 percent of the century's smelter output. The first zinc produced in the United States was smelted at the Government Arsenal in Washington, D.C., using ore from Franklin Furnace, N. J. The main U.S. zinc industry, however, did not start until about 1860, when successful smelters were erected in Illinois and Pennsylvania. From this time the industry boomed rapidly. Probably the most significant technological advance contributing to this surge was the successful commercial concentration of sulfide ores by froth-flotation processes shortly after the beginning of the 20th century.

Production of zinc for the world and for the United States from 1830 through 1970 is summarized in figure 77. Consumption of zinc (including secondary material) in the United States after 1937 also is shown. Before that time the United States had been virtually self-sufficient in zinc, and total domestic annual production generally exceeded consumption.

The record of world production is one of exponential growth since the end of the 19th century, inter-

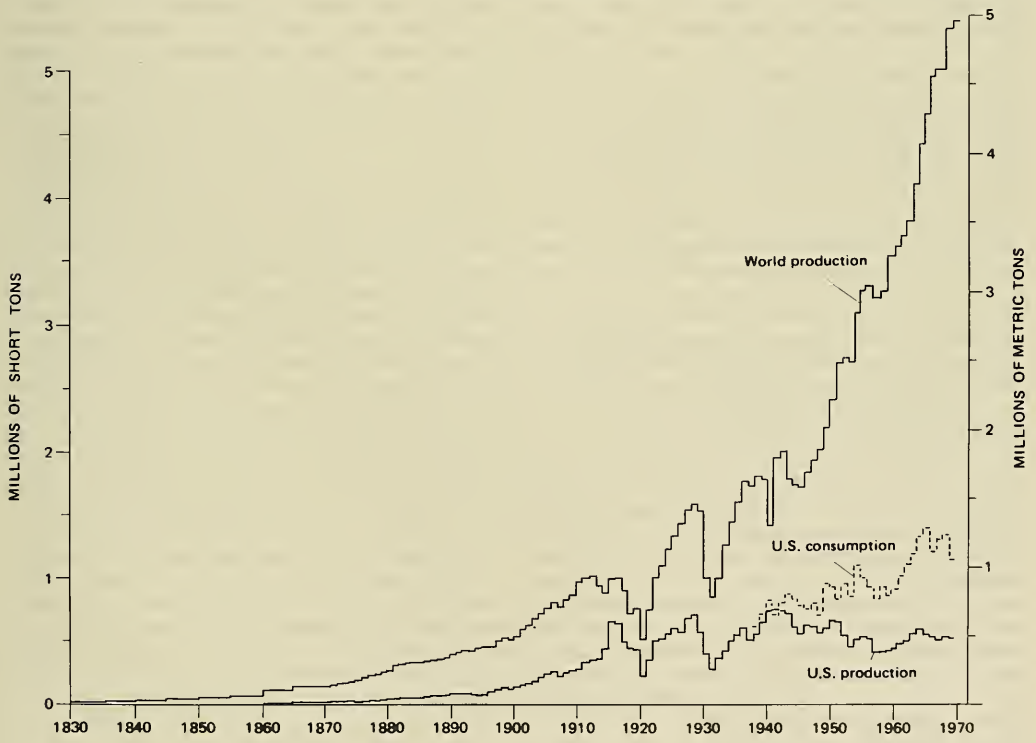

FIGURE 77.—Primary production of zinc in the world and in the United States, 1830–1970, and consumption of zinc, including scrap, in the United States, 1938–70.

rupted only by periods of political and economic stress, as during the First World War when Belgian, French, and Dutch smelter output was sharply curtailed, and during the 1918–22 economic depression which followed that war. The economic depression of the early 1930's is clearly reflected in the graphs for both world and U.S. production, and the effect of the outbreak of the Second World War on western European smelter output is reflected in world production decrease for 1941; U.S. production increased that year.

The most striking feature of the U.S. graph is that while consumption has grown consistently during and since the 1940's, mine production has remained nearly static, or has actually declined, so that during the period 1950–70 about half of U.S. needs have been met by imported materials, mainly ores and concentrates processed by U.S. smelters located near seaports. Increasing dependence on foreign zinc in recent decades has been due not so much to depletion of domestic deposits as to the lower cost of imported materials in relation to production costs at domestic mines. The U.S. imbalance will be aggravated further, at least through the mid-1970's, because of the closing of seven domestic zinc smelters between 1969 and 1972, brought about by obsolescence coupled with antipollution regulations.

Most significant is the fact that between 1950 and 1970 mankind consumed half of all the zinc produced in the world up to 1970, and between 1960 and 1980 will probably consume about as much zinc as was produced in all of history before 1960—that is, about 106 million short tons.

The year-to-year exploitation of zinc deposits will continue to be sensitive to economic conditions, but the probable trend will be one of growth, reflecting world population growth, increasing industrialization in developing nations, and the desire for a higher standard of living everywhere. However, the phenomenal increase in the production and consumption of zinc in the 20th century cannot continue indefinitely, and eventually production must decline as primary resources approach exhaustion. We believe that this point of irreversible decline is still several decades into the future, and is not likely to occur until the next century. Meanwhile, the industry, to prolong its survival, can be expected to seek improvements and innovations in mining and metallurgical techniques which will permit the exploitation of lower grade and unconventional types of deposits and the recovery of metal on a scale not previously possible, at the same time eliminating damage to the environment caused by current mining and smelting operations.

GEOLOGIC ENVIRONMENT

GEOCHEMISTRY

Zinc is a chemical element of atomic number 30 and atomic weight 65.38; it consists of the following isotopes: Zn^{64}, 48.89 percent; Zn^{66}, 27.81 percent; Zn^{67}, 4.11 percent; Zn^{68}, 18.56 percent; and Zn^{70}, 0.62 percent (Rankama, 1963, p. 579, 583). In fourfold coordination, zinc (Zn^{2+}) has an ionic radius of 0.71 A; in six-fold coordination, an ionic radius of 0.74 A (Green, 1959, table 2). These radii are close to those of Mg^{2+} (0.66 A), Cu^{2+} (0.72 A), and Fe^{2+} (0.74 A) (Green, 1959, table 2). Chemically, zinc is most similar to cadmium and mercury, the other two elements of Group IIb of the periodic system.

The range of estimates of the average crustal abundance of zinc is from 65 to 94 ppm (parts per million). It thus ranks ahead of copper (45–63 ppm) and lead (12–16 ppm), with both of which it is commonly associated in ore deposits. Mason (1958, p. 41) listed zinc as the 23d most abundant element in the earth's crust. Its concentration in igneous rocks varies from 130 ppm in basalts and syenites through values of 72 ppm in rocks of intermediate composition and 39–60 ppm in acidic rocks. The sedimentary rocks, such as sandstone, shale, and the carbonates, average 16 ppm, 95 ppm, and 20 ppm, respectively. Some carbonaceous shales are reported to contain as much as several thousand parts per million, whereas the Kupferschiefer of Europe may contain as much as 60,000 ppm, and although the average is something less, will contain several percent of combined copper-lead-zinc over large areas. Deep-sea clays reportedly average 165 ppm, and muds from the Atlantis II Deep in the Red Sea average 34,000 ppm. In western Canada, some dolomites may contain several thousand parts per million and in South Australia 1–2 percent zinc is reported as at least in part in solid solution in dolomite. (See Bischoff and Manheim, 1969; Dunham, 1964; Krauskopf, 1967; Muller and Donovan, 1971; Parker, 1967; Lee and Yao, 1970; Weber, 1964.)

Broad geochemical classifications of the elements generally group them as to (1) lithophile, siderophile, or chalcophile, and (2) oxyphile or sulfophile. Most lithophile elements rarely produce sulfide or related minerals in nature; they have a marked affinity for oxygen, and are enriched in the silicate crust or lithosphere. Chalcophile elements, conversely, have a strong attraction for sulfur, and siderophile elements are so named because they are enriched in the nickel-iron phase (siderosphere) as known from meteorites. The classification as oxy-

phile or sulfophile is related to the preference of an element for oxygen or sulfur, respectively. Thus, most lithophile elements are also oxyphile, most chalcophile elements are sulfophile, and many siderophile elements are either oxyphile, or sulfophile, or weakly both. Zinc seems to be a borderline case. While dominantly chalcophile, it also has some lithophile characteristics; and, although its dominantly chalcophile nature would suggest it to be sulfophile, it is classified as weakly oxyphile (see Rankama and Sahama, 1950, tables 4.3 and 5.4). This ambiguity is apparently due to its amphoteric nature—that is, the habit of its hydroxide to act as a weak base as well as a weak acid depending on the pH of the aqueous environment. In this respect it is like aluminum, beryllium, and gallium, but unlike iron and manganese. Thus, with increasing availability of hydroxyl ions, a solution containing zinc as the bivalent cation will precipitate $Zn(OH)_2$ at a pH of about 7–8. When the pH exceeds these values, the zinc reenters the solution, but as the zincate anion, ZnO_2^{-2}, or the hydrated zincate anion, $Zn(OH)_4^{-2}$. The reaction is reversible; as the pH of the solution decreases, the hydroxide is precipitated once again (pH 7–8) and is then redissolved as the bivalent cation with the further lowering of the pH. (See Krauskopf, 1955.)

The amounts of zinc in early magmatic sulfides are low, but zinc becomes concentrated in the residual solutions resulting from the continued differentiation of a magma, and these solutions in turn contribute to the concentrations in the pneumatolytic and hydrothermal phases so important in the genesis of ore deposits. On the other hand, small quantities of the metal remain behind with the various crystal phases of magmatic differentiation because of the diadochic capability of zinc to replace ferrous iron and magnesium in crystal structures. This replacement is possible because of the identity or near identity of the ionic radii of the three elements. Thus, trace quantities of zinc may occur in the early magmatic iron oxides, such as magnetite and ilmenite. Zinc apparently does not form separate silicate minerals in igneous rocks, although locally, certain species may be enriched in zinc sufficiently to be described as zincian varieties, (for example, amphibole, pyroxene, biotite, tourmaline, and garnet). Many of these zincian silicates, however, are more likely to be found in a metamorphic regime than in primary igneous rocks, such as, for example, the zincian biotites at Franklin Furnace and Sterling Hill, N. J. (Frondel and Einaudi, 1968).

Most primary ore deposits are formed in a relatively low pH environment. Consequently, most of the sulfophile ore metals are precipitated as sulfide minerals; hence the chief primary ore mineral of zinc is sphalerite, ZnS. During the weathering cycle, however, sphalerite is decomposed. Most of the zinc goes into solution as either the sulfate or the chloride and moves downward and generally away from the primary deposit, to be reprecipitated as carbonate, silicate, or other oxidized minerals depending on the availability of various anions in, and the chemistry of, the hydrologic regime. Zinc may be thus completely leached from the upper parts of primary zinc ore bodies or may be highly concentrated in the oxidized zone. Some chemical similarities of zinc to aluminum also suggest that zinc should be concentrated in bauxite. That this is not true is probably due chiefly to the low Zn-Al ratios in the rocks from which most commercial bauxite has been formed. However, where sufficient zinc is present, laterization may well result in a high-grade concentration not only of zinc carbonates and silicates but also of zinc-bearing clays and perhaps zincite.

ORE MINERALS

Many minerals contain zinc as a major component; 55 species of zinc minerals are listed by Dana (1945, p. 812). Native zinc is known but rare; Boyle (1961) listed reported occurrences in his description of native zinc in the oxidized zone at Keno Hill in the Yukon where it occurs with other native elements including sulfur. He attributes its occurrence there to the dissociation of sphalerite by autoreduction-oxidation processes.

The principal ore mineral of zinc is sphalerite, a zinc sulfide sometimes referred to as "blende" or "jack." Common varieties of sphalerite are yellow or resinous brown, although it may occur in other colors depending upon the type and amount of impurities. The pure and nearly colorless variety is known as cleiophane, whereas the dark-brown to black variety with more than 10 percent Fe is known as marmatite. Sphalerite crystallizes in the isometric system, whereas wurtzite, a relatively rare and less stable zinc sulfide, crystallizes in the hexagonal system. In some deposits the ore contains a banded intergrowth of sphalerite and wurtzite that is known as schalenblende. Trace metals associated with and recovered from zinc-sulfide concentrates include silver, cadmium, germanium, gallium, indium, and thallium.

Zinc sulfides oxidize readily to several secondary minerals, the more common of which are the zinc carbonate, smithsonite, and the hydrous basic zinc silicate, hemimorphite. The name "calamine" has been applied sometimes to several of the oxidized

zinc minerals, especially to hemimorphite, but it is not an approved mineral name. Franklinite, willemite, and zincite are the ore minerals of the renowned unique zinc deposits at Franklin Furnace and Sterling Hill, N. J. These minerals are uncommon elsewhere in the world; however, willemite is the chief zinc mineral in the recently discovered sizable deposits of Beltana and Aroona in the Flinders Range of South Australia; and willemite, zincite, hemimorphite, and hydrozincite constitute the ore minerals in the extensive deposit at Vazante in Minas Gerais, Brazil.

Some characteristics of the common ore minerals of zinc are given in table 152.

TABLE 152.—*Composition, zinc content, and selected physical characteristics of the common ore minerals of zinc*

Mineral	Composition	Zinc content (percent)	Specific gravity	Hardness	Crystal system
Sphalerite	ZnS	63–67	3.9–4.1	3½–4	Isometric.
Wurtzite	ZnS	59–67	4.0	4	Hexagonal.
Zincite	ZnO	75–80	5.7	4–4½	Do.
Franklinite	$(Fe,Zn,Mn)(Fe,Mn)_2O_4$	14–27	5.1	6	Isometric.
Smithsonite	$ZnCO_3$	48–52	4.3–4.4	5	Hexagonal.
Hydrozincite	$Zn_5(OH)_6(CO_3)_2$	59–78	3.6–3.8	2–2½	Monoclinic.
Willemite	Zn_2SiO_4	51–56	3.9–4.2	5½	Hexagonal.
Hemimorphite	$Zn_4(OH)_2Si_2O_7 \cdot H_2O$	52–54	3.4–3.5	4½–5	Orthorhombic.

Much zinc ore contains economically significant amounts of lead, copper, silver, and gold. Where present in the primary ores, the lead occurs as galena (PbS) and the copper as chalcopyrite ($CuFeS_2$). The silver is in solid solution in the galena or as exsolved traces of complex silver sulfides; more rarely, it accompanies the sphalerite. The gold is generally native, although it may also occur with silver in telluride minerals or in solid solution in some of the iron sulfides such as pyrite. Such mineralogically complex ores are typical of deposits formed in many areas of the Western United States during episodes of Tertiary and Cretaceous volcanism. They contrast markedly with other major zinc deposits, such as most of those of the Tennessee region, where the only sulfides are sphalerite and local lesser concentrations of pyrite, and where, in some deposits, barite or fluorite or both are significant coproducts or byproducts.

TYPES OF DEPOSITS

Zinc generally occurs with lead in many diverse geologic environments. The deposits have such different habitats and origins that they have been classified according to many different schemes. Within any mineralized district, area, or region there is generally more than one type of deposit, and it is not always clear where one type ends and another begins. Consequently, for the purpose of this report, zinc deposits, together with their associated lead and other elements, are classified by broad geologic environments as: (1) contact-metamorphic deposits; (2) irregular replacement deposits and associated fissure fillings; (3) vein deposits; (4) stratabound deposits in metamorphic rocks; (5) stratabound deposits in carbonate rocks (Mississippi Valley- or Alpine-type deposits); (6) stratiform deposits; and (7) deposits formed by supergene enrichment or laterization.

Ore deposits or mines containing or producing significant quantities of zinc, as the chief commodity, as a major coproduct, or as an important byproduct, are frequently classified by the associated metals, thus: (1) zinc; (2) zinc-lead or lead-zinc, depending upon which metal is dominant; (3) zinc-copper or copper-zinc; and (4) base metal, if all three metals are of about equal importance. If silver is also an important coproduct or byproduct, it too is added to the class designation.

CONTACT-METAMORPHIC DEPOSITS

Contact-metamorphic deposits, also known as contact-metasomatic or pyrometasomatic deposits, are those contained in metamorphosed sedimentary rocks adjacent to igneous intrusives. They are found chiefly in carbonate rocks that have been altered metasomatically to assemblages of silicated rocks commonly referred to as skarn, tactite, or garnet rock. Chalcopyrite, pyrite, pyrrhotite, sphalerite, and molybdenite are common ore minerals. The sphalerite is generally iron rich. The ore may be in tabular bodies parallel to bedding in the host rock, in irregular or pipelike bodies roughly conformable to the igneous contact, or in veins that transgress the metamorphosed host rock. Small irregular replacement deposits may occur in unaltered limestone some distance from the intrusives. Although many deposits of this type have been found in the United States, most are small and only a few have been significant producers. Examples include many of the zinc deposits in the Central district of New Mexico (Hernon and Jones, 1968) and those of the Darwin

district in California (Hall and MacKevett, 1962). Elsewhere in the world significant production has been won from this type of deposit at the Kamioka, Nakatatsu, Chichibu, and other mines in Japan, as well as at mines in northern China and Siberia. The Kamioka mine is the largest zinc-producing mine in Japan, yielding more than 25 percent of the country's annual zinc output. Other contact deposits producing zinc are in the Trepca district of Yugoslavia and in Sweden and Mexico.

IRREGULAR REPLACEMENT DEPOSITS AND ASSOCIATED FISSURE FILLINGS

In many mining districts the typical contact-metamorphic deposits just described are displaced outward or upward from the intrusive contact by deposits of obviously lower temperature. These deposits are irregularly shaped and are associated closely with filled fissures in either carbonate or clastic rocks. For the most part they appear to be both spatially and genetically related to intrusive igneous stocks of intermediate to acidic composition. Most are confined to zones where favorable strata are crossed by structural breaks. Some lie along veins, but irregular replacement bodies may extend considerable distances into certain beds of the wall rocks away from the veins. Locally, these bedded replacement bodies may be overlain and underlain by impervious shale or other less reactive rocks and may somewhat resemble the various stratabound deposits described below. They differ, however, in that they may occur throughout the local stratigraphic sequence as bedded replacements associated with adjacent veins, or as replacement bodies in pipelike structures that transgress the section. Ore from this type of deposit is more like that of ore in the classic vein deposits (described later) and contains, in addition to zinc and lead, appreciable quantities of copper, silver, and gold. Typical of these deposits in the United States are the silver-lead-zinc ores mined in the Park City, Bingham, and Tintic districts of Utah, at Leadville and Gilman, Colo., and in the Eureka district of Nevada. Elsewhere, examples include deposits in the Santa Eulalia and similar districts in Mexico, and in central Peru. (See Barnes and Simos, 1968; Rubright and Hart, 1968; Bush and others, 1960; Morris, 1968; Emmons and others, 1927; Radabaugh and others, 1968; Nolan and Hunt, 1968; Horcasitas and Snow, 1956; and Peterson, 1965.)

VEIN DEPOSITS

Veins are tabular ore bodies that fill faults or joints. The ore and accompanying gangue minerals either fill former open spaces along the fractures or replace the wall rock; commonly both modes of occurrence are recognized. Veins are narrow in width as compared with their length and depth; most have sharply defined walls. Zinc-bearing veins are not uniform in their metal content, and many have yielded more significant values in lead, copper, silver, and gold. Zinc-bearing veins are found in most kinds of rocks, although commonly they occur in igneous rocks or in rocks near igneous contacts. Veins containing sphalerite apparently form in a wide range of temperature and pressure conditions that are dependent upon the geologic environment. The minerals of the higher temperature veins may resemble those of the contact-metamorphic deposits, whereas the minerals of the intermediate to lower temperature veins will be generally similar to those in the lower temperature replacement deposits.

In the United States, important zinc-bearing veins have been mined in the Coeur d'Alene district of Idaho (Hobbs and Fryklund, 1968), at Butte, Mont. (Meyer and others, 1968), and at numerous localities in Colorado. Additional important zinc vein deposits occur elsewhere in the Western United States in many districts that are perhaps better known for other types of deposits. Well-known similar veins are found in several districts of central Europe, Italy, Mexico, and Peru. As widespread as vein deposits containing zinc apparently are, only a small portion of the world's production has been won from them, and they do not contain a significantly large part of the world's reserves and resources. (See also various papers in Ridge, 1968.)

STRATABOUND DEPOSITS IN METAMORPHIC ROCKS

Massive deposits of zinc-lead and zinc-copper ores occur in metamorphic rocks throughout the world. They consist, for the most part, of aggregates of pyrrhotite and pyrite accompanied by sphalerite, galena, and chalcopyrite. The ore bodies are lenticular masses parallel to stratification in enclosing metamorphosed sedimentary and interbedded volcanic rocks. Although deposits of this type are locally discordant to bedding or fill fissures that cut across the bedding or foliation, many evidently were originally bedded replacement deposits that were subsequently metamorphosed and folded. Some deposits of this type are in highly folded and faulted rocks, and although the ore replaces the host rock, the dominant feature of its control may be the faults and folds. These deposits include the largest concentrations of zinc-lead and zinc-copper ores that are known. Typical are those in the Broken Hill and Mount Isa districts of Australia, the Sullivan mine in British Columbia, the Bathurst district in New

Brunswick, and the Buchans mine in Newfoundland. Other stratabound massive sulfide deposits in metamorphic rocks have been mined in western Europe, as well as in various parts of Russia. Relative newcomers belonging to this very important class of zinc-bearing deposits include those at Prieska in South Africa and in Ontario and Quebec—for example, Kidd Creek, Mattabi, and Ruttan Lake. (See McLeod, 1965; Douglas, 1970; and South African Mining and Eng. Jour., 1972.)

Classified with the stratabound massive sulfides are that well-known Kuroko ores of Japan. Although these deposits are altered very slightly, if at all, they have most of the characteristics ascribed to this class of deposit. The Kuroko deposits range widely in size; some contain more than a million tons of zinc in ore consisting of fine-grained mixtures of sphalerite, galena, chalcopyrite, and iron sulfides.

Massive sulfide and other stratabound deposits in metamorphic rocks that have produced significant quantities of zinc in the United States are those in the Ducktown district of Tennessee, in the Jerome district of Arizona, in the Balmat-Edwards district of New York, and in the Franklin Furnace-Sterling Hill district of New Jersey. The latter two localities in New York and New Jersey differ from the others by being closely associated with Precambrian marble. The New Jersey deposits are almost unique among the major zinc deposits of the world in that the ore minerals are predominantly franklinite, willemite, and zincite rather than the more common, apparently ubiquitous, sphalerite. The New York and New Jersey districts together have produced more than 5 million tons of zinc and have resources of at least that much more.

STRATABOUND DEPOSITS IN CARBONATE ROCKS (MISSISSIPPI VALLEY- AND ALPINE-TYPE DEPOSITS)

Another major type of zinc-lead deposit is found in platform carbonate rocks in many parts of the world. In some, the ore minerals occur as open-space fillings in breccias; in others, the minerals formed chiefly by replacement. The ores in many districts are relatively low grade and occur as extensive bodies within broadly mineralized regions covering hundreds of square miles. They are classified as stratabound because they are confined to relatively thin zones, which are generally not more than several hundred feet thick, in much thicker carbonate sequences. Many districts are, for the most part, relatively undisturbed tectonically, as in the Mississippi Valley of the United States or in the Upper Silesian province of Poland. Elsewhere, as in the Appalachian and Alpine regions of North America and Europe, platform carbonates with their zinc deposits already in place have been deformed structurally by later tectonism. Although most of these deposits produce both zinc and lead, zinc is generally dominant. A major exception is the lead district of southeastern Missouri where the deposits contain about 5 percent lead, generally less than 1 percent zinc, and minor quantities of copper, silver, cadmium, cobalt, nickel, and germanium. This district contains one of the largest known concentrations of lead in the world. On the other hand, most of the deposits in some districts, for example, the major producing deposits of the East Tennessee districts and those of Middle Tennessee now being explored and developed, have only sphalerite and contain little more than trace amounts of galena. Other districts in the United States containing stratabound deposits in carbonate rocks are the Upper Mississippi Valley district of the Wisconsin-Illinois region, the famed Tri-State district in Kansas, Missouri, and Oklahoma, and the Friedensville district in eastern Pennsylvania. The major deposits in the Metaline district in northeastern Washington are also considered to be of this type, although they appear to be much more structurally disturbed and metamorphosed than the previously mentioned deposits. Elsewhere, examples of significant deposits of this type are at Pine Point in western Canada; in several countries in northwestern Africa; in the European Alps from France eastward through Italy, Austria, and Yugoslavia; and in the Upper Silesian district of Poland. The Broken Hill district in Zambia, the Balmat-Edwards district in New York, and the Franklin Furnace- Sterling Hill districts in New Jersey are considered by some investigators to be highly altered or metamorphosed equivalents of this class. (See various authors in Ridge, 1968; also in Brown, 1967, and in Wedow and others, 1971.)

STRATIFORM DEPOSITS

The stratiform deposits containing zinc have also been referred to as stratabound deposits of syngenetic or diagenetic origin or simply as sedimentary deposits. *Stratiform* deposits should not be confused with *stratabound* deposits. Stratiform indicates the deposit is in the form of a stratum interbedded with other strata, for example, the Clinton-type sedimentary iron ores, whereas stratabound deposits may be crosscutting but are confined to a zone bounded by strata. In a general sense, all stratiform deposits are stratabound, but not all stratabound deposits are stratiform. (Note: Usage of the terms *stratabound* and *stratiform* in this chapter is somewhat different from usage in some chapters.—Eds.)

Perhaps the most significant known occurrence of this type is the famed Kupferschiefer, chiefly in East Germany, but extending from England eastward to Poland. This is a bed of carbonaceous shale generally less than 1 meter thick that contains several percent combined copper, lead, and zinc as finely disseminated sulfides. This mineralized bed is more than 20,000 square kilometers in areal extent and occurs in the basal part of the Permian Zechstein Formation of East Germany or its equivalents. Copper is more abundant than zinc and lead in some beds, and zinc and lead are more concentrated than copper in others. Where the Kupferschiefer has been mined for copper, the zinc content is less than 1½ percent. Elsewhere, as at Uftrungen and near Bottendorf, the zinc content is higher, being about 1.7 and 3.2 percent, respectively.

Other zinc-bearing stratiform deposits seem to be rare. Some investigators believe the deposits at Tynagh, Eire, have a sedimentary origin, although others cite contrary evidence. It is possible that other stratiform deposits exist among oil shales or other carbonaceous sediments elsewhere in the world. As much as 1 percent Zn is reported in a variety of black shales around the world (Tourtelot, 1970). Another possibility of zinc occurrence is in evaporite sequences where zinc might occur in minerals other than sulfides. This suggestion is raised by the occurrence of several tenths of a percent zinc in samples of Devonian and Triassic dolomites associated with evaporite sequences in Alberta and elsewhere in western Canada (Weber, 1964) and associated with the modern evaporites of Lake Eyre in South Australia (Davidson, 1965). The sphalerite nodules in the Middle Silurian dolomites of southern Ontario (Sangster and Liberty, 1971) might also be classified as being of diagenetic origin in stratiform deposits.

DEPOSITS FORMED BY SUPERGENE ENRICHMENT OR LATERIZATION

Much has been written about the supergene enrichment of silver-bearing base-metal deposits, chiefly those occurring in the Western United States. Such enrichment in the weathered parts of primary ore deposits is generally not considered to be a separate type of deposit but only a process by which a lower grade primary sulfide ore or protore is made exploitable by chemical reconcentration during weathering. Most of the zinc ores mined until the early part of the 20th century were from such oxidized deposits (Heyl and Bozion, 1962). Most of these deposits were clearly formed by decomposition of sulfides in the bedrock during a weathering cycle, when the metals were redeposited nearby as carbonate, silicate, or oxide minerals or as secondary sulfides if they were in a reducing environment. In many places, as early mining exhausted these enriched supergene products, the nearly one-to-one relation with primary sulfide occurrences in bedrock was evident. In the Western States (Heyl, 1963, 1964) many secondary zinc deposits clearly were formed by alteration of the primary sulfides virtually in place or by direct replacement of limestone by smithsonite or hemimorphite from zinc-bearing solutions. However, in the Appalachian region, the oxidized zinc deposits were formed as accumulations of smithsonite and hemimorphite in saprolitic clay pockets between pinnacles of the carbonate bedrock. According to Heyl and Bozion (1962, p. A19–A21), the zinc came from primary disseminations of sphalerite previously deposited in the unweathered carbonate host. These zinc-rich saprolites are analogous to the terra rossa-type residual aluminous or ferruginous laterite pockets formed by the deep weathering of impure limestone.

Until the advent of successful froth-flotation processes shortly after the beginning of the 20th century, sulfide ores containing sphalerite could not be concentrated economically, and most zinc mined in the world was obtained from the oxidized deposits. Major districts producing such ores in the United States included Friedensville, Austinville, Embreeville, Mascot, and Jefferson City in the Appalachian region and Leadville, Tintic, Ophir, and Cerro Gordo in the Western States. Much of the early production in the districts of the Mississippi Valley region was also from the enriched ores of the oxidized zone. (See Heyl and Bozion, 1962.) Significant amounts of this type of ore were also mined in Belgium, Germany, and Poland, as well as in Africa.

In contrast to the enrichment of zinc ores obtained in temperate climates, where the zones of oxidation are shallow, are the enriched oxidized ores of zinc found in tropical-weathering regimes. Here, the oxidized ores are perhaps best likened to laterites in that the process forming them, in effect, is laterization. Perhaps one of the best documented deposits that can be classified as a zinc-bearing laterite is that at Vazante in Minas Gerais, Brazil. This deposit is estimated to contain more than 5 million tons of zinc; lead, copper, and vanadium may also be recoverable. Carvalho and others (1962) have described the Vazante deposit and the exploration of it during the 1950's. Epigenetic zinc, lead, and copper(?) sulfides in a lower Paleozoic rock were decomposed by weathering, with the development of a strong ferruginous gossan (chapeau de ferro).

Beneath the gossan, an enriched zinc deposit was formed by the deposition of willemite and other secondary zinc minerals; some galena and sphalerite were replaced by supergene chalcocite. Continued weathering further enriched the zinc, with the formation of hemimorphite and hydrozincite on a major scale. Further alteration followed, with the consequent formation of zincite and additional hydrozincite.

The latter stage of enrichment probably began at some time during the Tertiary, and it continues today with additional concentration being effected by eluvial processes. The formation of the zincite and hydrozincite in the last stage strongly suggests the desilication process so typical of the last stage of laterization in the formation of the bauxite and iron and manganese oxide ores in the tropics. It is now an easy step of speculation to concur with the hypothesis of Rastall (supported by Palache, 1935, p. 23–24) that the Franklin Furnace-Sterling Hill oxide-silicate ore in New Jersey is merely a metamorphosed ancient iron-manganese-zinc laterite.

Other high-grade oxidized ore deposits found in the tropics are at Broken Hill in Zambia, one of the larger zinc deposits in the world; and one recently discovered and being developed in the Pa Daeng Mountains of Thailand. The Thai deposit is reported to contain about 3⅓ million tons of ore containing 35 percent zinc formed by the " * * * secondary replacement [of] limestone, sandstone, and shale by smithsonite, calamite [hemimorphite], hydrozincite, and zinc-bearing clays" (Eng. and Mining Jour., 1972). The previously mentioned high-grade willemite replacement deposits in Cambrian dolomite in the Beltana district of South Australia are also considered tentatively as having been formed by Tertiary supergene enrichment; although no association with primary sulfides has yet been discovered, Muller and Donovan (1971, p. 233) reported 1–2 percent zinc in weakly mineralized limestone with some of the zinc in solid solution in dolomite. Also, " * * * Tertiary lateritic material, which overlies the limestone in places * * * appears to be capable of adsorbing up to 2 percent Zn."

RESOURCES

Table 153 lists currently estimated zinc resources of the world, subdivided into recoverable and subeconomic and into identified and undiscovered; it also compares these classes of resources of the United States with those of the rest of the world.

Erickson (Crustal abundance chapter) indicates that the zinc content of the earth's crust is 2,250 $\times$ 10^{12} metric tons, of which 1,220 $\times$ 10^{12} metric tons is in the total continental crust of the world, of which 73 $\times$ 10^{12} metric tons is in the continental crust beneath the United States. Within a depth of 1 kilometer (approximately 3,000 ft) the continental crust contains 34 $\times$ 10^{12} metric tons of zinc, of which 2 $\times$ 10^{12} metric tons is within the United States. Erickson further estimates that the world reserve (recoverable identified resources) potential is 3,400 million metric tons, of which 198 million is in the United States. These latter tonnages are for ores averaging 4-percent zinc and, for the most part, presumably of the conventional sulfide type currently being exploited. Although the figures presented are highly speculative, they represent an expectable order of magnitude.

TABLE 153.—*Identified and undiscovered zinc resources of the United States and the world (estimated in millions of metric tons)*

	Identified resources [1]	Undiscovered resources	Total
United States			
Recoverable	[2] 45	60	105
Subeconomic	[3] 75	230	305
Total	120	290	410
Rest of the world			
Recoverable	[2] 190	285	475
Subeconomic	[3] 1,200	3,000	4,200
Total	1,390	3,285	4,675
Total world			
Recoverable	[2] 235	345	580
Subeconomic	[3] 1,275	3,230	4,505
Total	1,510	3,575	5,085

[1] IDENTIFIED RESOURCES: Specific, identified mineral deposits that may or may not be evaluated as to extent and grade, and whose contained minerals may or may not be profitably recoverable with existing technology and economic conditions.
[2] RESERVES: Identified deposits from which minerals can be extracted profitably with existing technology and under present economic conditions.
[3] CONDITIONAL RESOURCES: Specific, identified mineral deposits whose contained minerals are not profitably recoverable with existing technology and economic conditions.

Comparison of the data in table 153 with those of Erickson suggests that neither the United States nor the world as a whole has yet reached its potential for "high-grade ores." The total of estimated identified and undiscovered recoverable zinc resources of the United States, 105 million tons, is about one-half of Erickson's potential 200 $\times$ 10^{6} metric tons, whereas those of the world are estimated at only about one-seventh of his world potential of 3,400 $\times$ 10^{6} tons.

Most of the newly discovered recoverable zinc resources found in the last few years have been largely in deposits of two types, the stratabound deposits in metamorphic rocks (massive sulfide ores) and the stratabound ores in carbonate rocks (Mis-

sissippi Valley-type deposits). T. H. Kiilsgaard and B. A. LaHeist (written commun., 1962) showed in their estimate of resources that these two types of deposits each contain about one-third of the total. Furthermore, their estimate indicates that replacement, vein, and contact-metamorphic deposits, in that order, dominate the remaining third of the recoverable resources. They did not list separately the deposits herein designated as stratiform and as formed by supergene enrichment or laterization. Bachau (1971, p. 8–10) estimated that the massive sulfide ores and the Mississippi Valley-type deposits contain more than two-thirds of the total of exploitable zinc. Announcements in recent mining magazines show that most of the major new discoveries belong to these two major types of deposits, and much of the undiscovered recoverable zinc resources is in these categories. However, other announcements give credence to the belief that oxidized deposits formed by laterization may be a category to exploit. This type of deposit holds the promise of large, shallow, high-grade, nonsulfide ores, examples of which are the deposits at Vazante in Brazil, in the Pa Daeng Mountains of Thailand, and in the Beltana district of South Australia. All these deposits are under development, if not in actual production.

Recoverable identified resources of the United States are listed by major geologic regions in table 154, and those of the world are given by continent in table 155.

TABLE 154.—*Recoverable identified zinc resources of the United States grouped by major geologic regions*

Region	Zinc content (millions of metric tons)
Appalachian [1]	16.4
Mississippi Valley [2]	19.2
Rocky Mountain [3]	7.3
Pacific Coast [4]	2.1

[1] Chiefly the Franklin-Sterling Hill, Friedendsville, and Edwards-Balmat districts in New Jersey, Pennsylvania, and New York, as well as the Austinville-Ivanhoe district in Virginia and the several East Tennessee districts.

[2] Chiefly the Tri-State and Upper Mississippi Valley districts and the Missouri lead belts; also includes large inferred (possible) recoverable resources in the newly developing Middle Tennessee districts.

[3] Major sources include the Butte district in Montana; the Gilman, Leadville, and several smaller districts in Colorado; the Eureka, Pioche, and White Pine districts in Nevada; the Bingham, Park City, and Tintic districts in Utah; the Central, Pecos, and Mogollon districts in New Mexico; and the Big Bug, Bisbee, and Verde districts in Arizona.

[4] Chiefly the Metaline and Northport districts in Washington and the Coeur d'Alene district in Idaho; includes small districts in California, Oregon, and Alaska.

The total of identified subeconomic (conditional) resources and both recoverable and subeconomic undiscovered resources is given as 4,850 million metric tons of contained zinc (table 153). Tonnage of selected examples of the types of zinc occurrences that contribute to this total are presented in table 156.

TABLE 155.—*Recoverable identified zinc resources of the world*

Continent	Zinc content (millions of metric tons)
North America	84
South America	16
Europe	58
Africa	14
Asia	42
Australia	21
Total	235

TABLE 156.—*Selected examples of types of zinc occurrences that contribute to the total of conditional[1] and undiscovered zinc resources of the world*

Example	Zinc content (millions of metric tons)
Kupferschiefer of Europe	1,000
Deep-sea manganese nodules	750
Metal-bearing Red Sea muds	3
Deep-lying zinc deposits in Washington State	24
Zinc-bearing pyrite at United Verde mine, Arizona	1
Deposits in platform carbonate rocks:	
1) Mississippi Valley-type deposits	600
2) Zinc in dolomitic evaporites and related deposits	700
Paleoequivalents of Red Sea muds	60
High-grade lateritic ores	30
Zinc byproduct from manufacture of fertilizer from selected phosphorites	5
Zinc coproduct or byproduct from massive sulfide or kuroko type deposits	300

[1] CONDITIONAL RESOURCES: Specific, identified mineral deposits whose contained minerals are not profitably recoverable with existing technology and economic conditions.

Among the known lower grade or subeconomic zinc resources are the extensive deposits of the Kupferschiefer and related beds in the Permian Zechstein Formation of Europe (Dunham, 1964). Resources in these beds must exceed 1 billion tons of zinc; in one area alone in East Germany, Richter-Bernburg (1941) estimated the contained zinc at 200–250 million tons, and comparable though lesser quantities of lead and copper accompany the zinc. An example of the type of deposit that remains as a resource until beneficiation or other extractive techniques are improved is the zinc-bearing pyrite at the United Verde mine in Arizona, where about three-fourth million tons of zinc occurs in 12 million tons of pyritic ore (Anderson and Creasey, 1958). Other subeconomic types of deposits with significant zinc resources are mineralized bodies of relatively low tenor but of the same type as those currently being mined from carbonate rocks in the Mississippi Valley and Appalachian regions of the United States and elsewhere in North America. The resource potential for this type of deposit in North America must exceed several hundred million tons of zinc, particularly if that for the East Tennessee and the newly discovered Middle Tennessee districts is esti-

mated at a total of about 50 million tons of contained metal.

As mentioned previously, deposits formed by laterization may have a high resource potential, although this type of deposit has not been sought specifically with the persistence given to the search for massive-sulfide and Mississippi Valley-type ores. More likely the so-called zincian laterites will be found in tropical regions, although ancient tropical regimes might also be sought among older geological terranes. Geochemical search techniques would be as appropriate for ores of this type as for the more conventional sulfide types (Muller and Donovan, 1971).

Some potential resources await the development of unconventional mining and beneficiation techniques. Such resources include metal-bearing muds (Degens and Ross, 1969) and manganese nodules (Mero, 1962, 1965) on the sea floor. Muds in the Atlantis II Deep of the Red Sea contain an estimated 2.9 million metric tons of zinc deposited from hot brines (Bischoff and Manheim, 1969). The more than 1½ trillion tons of manganese nodules in the Pacific Basin, that have an average content of 0.05 percent zinc and 0.1 percent lead, are expected to contain about ¾ and 1½ billion tons of zinc and lead.

Evaporite deposits are another potential but unconventional source of zinc. Weber (1964) reported several tenths percent zinc in samples of dolomite associated with Devonian and Triassic evaporite sequences in Alberta and elsewhere in western Canada. Davidson (1965), in discussing the association of stratabound sulfide deposits with evaporite sequences, cited the occurrence of a 2½-foot zone that has a content of 0.2 percent Zn in the modern evaporites of Lake Eyre in South Australia.

PROSPECTING TECHNIQUES

As with other metallic minerals, four main techniques are used in the search for new deposits of zinc: geological, geochemical, geophysical, and direct physical.

The geological method consists primarily of plotting on a base map the distribution and character of all rocks in the area studied. Geologic structures such as bedding, foliation, faults, joints, and other features also are plotted, in addition to the boundaries between formations. Indications of rock alteration other than weathering, especially signs of mineralization, are also mapped. Discoveries of new ore bodies or extensions of old ones determined by geologic investigation are commonplace. (See Kiilsgaard, 1965.)

Geochemistry is a relatively new exploration tool that has become widely used in recent decades. Samples of soil, rock, and stream sediment are taken systematically and analyzed for zinc and other trace elements by colorimetry, spectrography, atomic-absorption spectrometry, or other analytical technique. Geochemistry is particularly useful in eliminating areas of low potential and selecting favorable targets in areas of anomalously high metal concentration. (See Hawkes and Webb, 1962).

Geophysical techniques depend upon contrasts between ore bodies and their surrounding rocks in certain physical properties such as magnetic, electrical, or gravimetric properties, or in response to seismic waves. Most physical properties of zinc minerals do not contrast sharply with those of their host rocks; thus, geophysical methods are useful in the search for zinc only to the extent that other minerals or special conditions are present in the ore body which do respond to the instruments employed. For example, magnetite and pyrrhotite, if sufficiently abundant, give a magnetic response, whereas pyrite, chalcopyrite, galena, and other sulfides commonly associated with sphalerite respond to self-potential, induced-polarization, resistivity, electromagnetic, and audiofrequency magnetic methods. Massive sulfide ore bodies also may be detected by gravimetry. Commonly, two or more geophysical methods are employed simultaneously, and airborne instruments have proved to be outstandingly useful. (See Dobrin, 1960; Parasnis, 1966; Soc. Explor. Geophysicists, 1966, 1967).

Although the geological, geochemical, and geophysical techniques have been discussed separately, they are most productive when used together. The geology is fundamental, but geochemical and geophysical methods have proved so useful as to become standard in most comprehensive exploration programs. A common procedure is to perform the geological and geochemical investigations first, and then the geophysical technique on selected targets. In vast drift-covered areas, as in Canada, airborne geophysical investigations often precede the geological and geochemical. Ultimately, however, a discovery is made only by direct physical means such as drilling, trenching, test-pitting, stripping, sinking a shaft, or driving an adit. The other three techniques are but a preclude to this most expensive final exploration step and are useful only to the extent that they reduce costs by picking the most favorable targets. In general, a direct physical method should be used as soon as a favorable target is indicated by one or more of the three less direct techniques. (See McConnel, 1965.)

PROBLEMS FOR RESEARCH

Although a high potential for zinc resources in all categories seems apparent, research is needed on zinc and zinc-bearing deposits in all fields of the geosciences to improve search techniques. More imaginative thinking is necessary in the search for conventional types of deposits to develop new concepts that can improve our understanding of geologic features localizing ore bodies and districts and also the sources of the mineralizing fluids. Most conventional deposits are considered to form during a single period of mineralization and then to remain isolated from later geologic processes until discovery. It is not logical to believe that deposits formed hundreds of millions of years ago have remained unchanged by the various geologic environments through which they have passed. Many ore deposits may be more ephemeral than their host rocks and in some environments could have been completely or partially resorbed by new migrating brines. The metals were precipitated from these new brines to form new ores or were dispersed into surface waters eventually to reach the sea. Search for evidence of such removal, particularly if only in part, and the tracing of the path of the brine migration, might well lead to the discovery of the later and possibly more enriched ores. Such solution and redeposition concepts may be particularly fruitful in exploration for Mississippi Valley-type ores. Furthermore, the metal-bearing brines, regardless of their source, may have moved laterally many miles through ancient carbonate aquifers to be trapped in large reservoirs where different geochemical conditions precipitated the metal.

Further studies of geophysical techniques are needed in the search for zinc-bearing ores. The application of magnetic and electromagnetic techniques are reasonably well understood. On the other hand, gravity and seismic techniques have not been pursued to any great extent. This may be largely because they have been tried with no immediate success or because they have been considered and discarded on theoretical grounds, with no extensive experimental studies. Gravity surveys may be particularly useful in locating large breccia bodies of the Mississippi Valley type when concealed under a relatively shallow cover. Another application of gravity studies could be in the search for extensions of high-grade zinc laterites under cover of dense tropical vegetation.

A better understanding of zinc geochemistry and the geochemistry of potential environments of deposition is of prime importance. The amphoteric nature of zinc and its role in the formation of oxidized zinc deposits need further consideration. The anomalous amounts of zinc in certain evaporitic rocks need explanation to determine if further enrichment in evaporites is possible—also whether such enrichment, if stripped from its host, might be a source of metal in ore fluids. Further investigation of zinc geochemistry as applied to exploration investigations will also be valuable. Simplification of field analytical methods would be helpful for exploration geochemical surveys in remote areas.

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ZIRCONIUM AND HAFNIUM

By Harry Klemic, David Gottfried, Margaret Cooper, and Sherman P. Marsh

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ABSTRACT OF CONCLUSIONS

Zirconium and hafnium are metals that are useful principally in metallic form in the chemical and nuclear reactor industries and in mineral form as zircon ($ZrSiO_4$) in the metal foundry and glass industries. Zircon and baddeleyite (ZrO_2) are the principal sources of zirconium, and hafnium is recovered in extracting reactor-grade zirconium. Both metals are reduced by the Kroll process.

Zircon and baddeleyite occur as primary minerals in alkaline-rich igneous rocks, but zircon is recovered mainly from titanium-bearing placer sands. The United States is a major producer and consumer of zircon and imports large quantities from Australia, which is the world's largest producer of zircon. Identified resources of zircon in the United States are about 10,800,000 short tons, of which nearly 80 percent is in the Atlantic Coastal States. U.S. production is solely from Florida and Georgia, as a byproduct of titanium production.

World identified resources exceed 36 million short tons of zircon equivalent. World production of zirconium concentrates in 1970 was more than 450,000 tons. Of this, the the United States used about 30 percent. Current supplies of zircon exceed demand for a few decades, but environmental problems may limit mining of some placers in the near future. Research is needed to find alternate sources and means of extracting zirconium minerals.

INTRODUCTION

Zirconium and hafnium are elements that in their metallic forms are principally useful in the chemical and nuclear-reactor industries, in applications for which corrosion resistance, structural stability at high temperatures, specific alloying properties, or specific neutron-absorption characteristics are required. About 8 percent of all the zirconium consumed in the United States is used in these industries (Stamper and Chin, 1970a, b). The most common naturally occurring zirconium- and hafnium-rich mineral, zircon ($ZrSiO_4$), which generally con-

tains nearly 49 percent zirconium and less than 2 percent hafnium, is the principal source of these elements. Baddeleyite (ZrO_2), a commercially important but less abundant zirconium-rich mineral, contains approximately 73 percent zirconium and 1 percent hafnium (Kauffman, 1956). Because of their refractory nature (melting points 2550°C or greater), these minerals are useful directly as mold materials for casting ferrous metals in foundries and in bricks and blocks in glass furnaces. Of an estimated total U.S. consumption in 1970 of 145,000 short tons of zircon concentrates, 100,000 tons was for foundries, 22,000 tons for refractories, and 23,000 tons for other uses (Clarke, 1970). Zircon, both natural and synthetic, is also used in minor quantities as a gemstone.

Zircon is processed as an industrial mineral by reacting it with dolomite at high temperatures to produce zirconia (zirconium dioxide, ZrO_2), which has a higher melting point and is less reactive than zircon in some metallurgical systems. Zirconium compounds for other uses are prepared from zirconium oxide (Stamper and Chin, 1970b).

ZIRCONIUM AND HAFNIUM METALS

Zirconium metal is obtained by reacting zircon with coke in electric furnaces to produce zirconium carbonitride, which is chlorinated to zirconium tetrachloride. The Kroll process, which involves reduction of the tetrachloride by magnesium metal in an inert atmosphere, is used to obtain zirconium sponge metal which contains about 2 percent hafnium. Metal fabricated from the sponge is suitable for non-nuclear applications (Stamper and Chin, 1970b).

Both zirconium and hafnium metals have excellent structural properties and resistance to corrosion at elevated temperatures, which make them particularly useful in reactor materials in which these properties are required.

Reactor-grade zirconium and hafnium metals are produced by dissolving crude zirconium tetrachloride, which contains some hafnium, and chemically separating the hafnium from the solution. The zirconium and hafnium components are separately processed to form chlorides which are reduced to metals by the Kroll process. The necessity to separate the zirconium and hafnium to meet the requirements for reactor-grade metals arises from the different nuclear properties of the two metals. Zirconium, having a low neutron absorption cross section (less than 0.2 barn), is useful in reactor components in which minimum neutron absorption is required. Hafnium, which has a relatively high neutron absorption cross section (105 barns), is useful in components in which neutron absorption is a desired property (Weast and others, 1965; Lustman and Kerze, 1955).

USES OF ZIRCONIUM

In addition to its principal use for structural materials in nuclear reactors, zirconium metal is used in small quantities in camera flashbulbs to provide quick ignition and longer light intensity. Zirconium alloys are used for making mechanical components such as heat exchangers, valves, tubing, spinnerets, and crucibles for the chemical industry (Stamper and Chin, 1970b). Zirconium-columbium alloys are used in superconducting magnets. Zirconium compounds are also used in ferroalloys, glazes, enamel, welding rods, abrasives, pharmaceuticals, paints, and water repellents, and for sandblasting.

Zircon and zirconium metal and compounds have many substitutes in their various applications. Chromite and other materials are substitute mold materials. Titanium oxide and tin oxide may be used in place of zirconium oxide in opacifiers for ceramic glazes and enamels. Other metals and alloys, such as those of titanium, tantalum, and stainless steels, may be used in place of zirconium metal and alloys. Substitution of other materials for zirconium materials is based upon specific performance, price, availability, and other factors.

USES OF HAFNIUM

The principal use of hafnium is in the form of metal, mainly for control rods for nuclear reactors. A minor amount is used as an additive in alloys, and, in recent years, about 15 percent of the hafnium used in the United States was used as the oxide, mainly for research. Hafnium has been used in electric light bulbs and in electrodes in X-ray tubes and other electronic tubes. Numerous other uses of hafnium have been investigated (Stamper and Chin, 1970a). Alternate materials for hafnium for nuclear-reactor control rods are stainless steels containing silver, indium, cadmium, boron, and rare-earth elements.

PRODUCTION

Zircon, the principal raw material for the extraction of zirconium, is available in excess of demand. Zircon production is directly related to the production of titanium mineral concentrates from placer sand deposits. Australia, the leading producer of concentrates of titaniferous sands, is also the leading producer of zircon concentrates. The production of zirconium concentrates in recent years from five nations is given in table 157. (U.S. production figures are withheld to avoid disclosing individual company confidential data.) Zircon production capacity in

TABLE 157.—*Production, in short tons, of zirconium concentrates from five nations, 1968–70*

[e, estimate; NA, not available Data from Clarke, 1970]

Country	1968	1969	1970
Australia	332,956	411,021	e403,000
Brazil	3,083	3,874	NA
Ceylon	28	75	123
Malaysia	[1] 1,241	[1] 1,562	[2] 998
Thailand	3,549	276	[2] 2,469
Total	340,857	416,808	406,590

[1] Exports of zircon.
[2] Exports of zircon and zirconium sand to Japan.

India and Ceylon was expected to be near 10,000 and 9,500 tons per year, respectively, by the end of 1970. The zircon production capacities of Malaysia, South Africa, and the United Arab Republic were reportedly small. Total world production of zirconium concentrates, including unreported amounts of baddeleyite, zircon , and eudialyte, probably exceeded 500,000 short tons.

The combined zirconium and hafnium contents of zircon concentrates form approximately 50 percent of the tonnage. The ratio of zirconium to hafnium in the concentrates is about 50 to 1. Total world production of zirconium in 1968 was estimated by the U.S. Bureau of Mines to be about 247,000 short tons (Stamper and Chin, 1970b). This total was based upon reported production and upon assumed amounts of 30,000 tons for the U.S.S.R. and 39,000 tons for the United States. Data on actual production for these countries and for Japan and India are not available. Because production in Australia increased by about 34,000 tons of zirconium between 1968 and 1971, world production in 1971 is estimated to have been approximately 280,000 short tons.

ESTIMATED U.S. PRODUCTION OF ZIRCONIUM CONCENTRATES

United States production of zircon is solely from the Trail Ridge area, Florida, and Folkston, Georgia. Zircon and zirconium products are processed in several states. Specific production data are not released, but the order of magnitude of their production can be estimated. Stocks of zircon held by dealers and consumers in the United States, exclusive of those held by foundries, during the years 1968–71 have varied only slightly; so the difference between the amounts imported and the total U.S. consumption, as shown in figure 78, indicates the order of magnitude of domestic production. The data suggest a decrease from 83,000 short tons estimated for 1968 to between 50,000 and 55,000 tons in 1970 and 1971, depending upon the source of the zircon exported from the United States, and the amount of zircon reused.

PRODUCTION OF ZIRCONIUM AND HAFNIUM

Zirconium metal production in the United States in 1968 was entirely from imported concentrates. Data concerning the amount produced are not available. Hafnium demand in that year, about 18 short tons, was met by processing imported zircon to produce hafnium-free zirconium. Hafnium crystal bar production in 1970 was 35 short tons (Clarke, 1970).

PRICES

The prices of zirconium and hafnium raw materials and of various products of these elements are indicated in the following list, from data compiled by the U.S. Bureau of Mines from published sources for 1970 (Clarke, 1970):

Specification of material	*Price*
Zircon:	
Domestic, per short ton, f.o.b. Starke, Fla. (minimum 66 percent ZrO_2)	$ 56.00–$57.00
Imported, sand, per long ton, in bags, c.i.f. Atlantic ports (minimum 65 percent ZrO_2)	70.00
Zircon and zirconia brick, 9-inch equivalent brick, per brick	3.72
Zirconium oxide, in various grades and lots, per pound	0.41– 1.50
Zirconium:	
Powder, per pound	12.00– 13.00
Sponge, per pound	5.50– 7.00
Hafnium:	
Sponge, per pound	75.00
Bar and plate, rolled, per pound	120.00

It is apparent that the price of about 3 cents per pound for the zircon is only a small part of the price of the various prepared products. The difference in prices is related to the complexity and cost of the processes required to convert the zircon to usable products.

TRADE

The average value of imported zircon, 92 percent of which was from Australia in 1970, was $39.08 per short ton, and the total value of zircon imported into the United States was $3.7 million (Clarke, 1970). Products of zirconium and hafnium valued at approximately $1.6 million were imported into the United States in 1970. These were from Canada, France, West Germany, Switzerland, Netherlands, United Kingdom, and Japan. U.S. imports for consumption of zircon were from Australia, Canada, Republic of South Africa, and the United Kingdom. The value of zircon imports from Australia was nearly $3.3 million. Some sales contracts for rutile from Australia stipulate that zircon must also be purchased in some proportional quantity (Stamper and Chin, 1970b).

FIGURE 78.—U.S. consumption, imports, and exports of zirconium concentrates, 1944–71. Figures for U.S. total consumption for 1963–66 not available. Data from U.S. Bur. Mines "Minerals Yearbooks, 1944–70" and "Commodity Data Summaries, 1972."

The United States exported nearly $6.9 million worth of zirconium ores, concentrates, and zirconium-bearing materials to 30 countries on all the continents. Exports to Canada were valued at $3 million.

Although the United States imports a considerable

amount of the zircon it consumes, domestic resources of zircon are large and could be utilized in greater quantities if foreign supplies were not available. World resources of zircon are sufficient to meet the demand in the foreseeable future. A better understanding of the zirconium and hafnium resources of the world can be obtained by an examination of the geologic occurrence of these elements.

GEOLOGIC ENVIRONMENT

GENERAL GEOCHEMICAL AND MINERALOGIC CONSIDERATIONS

Zirconium and hafnium have long been recognized as a classic example of a pair of geochemically coherent elements; that is, they invariably occur together in rocks and minerals. Their close association is explained by their nearly identical charge, ionic radii, electronegativity, and ionic potentials (table 158).

TABLE 158.—*Selected data on zirconium, hafnium, and geochemically associated elements*

[Data from Green, 1959, table 2]

Ion	Atomic No.	Ionic radius	Electronegativity (kilocalories/gram-atom)	Ionic potential
Zr^{4+}	40	0.79	200	5.08
Hf^{4+}	72	.78	180	5.12
Th^{4+}	90	1.02	170	3.92
U^{4+}	92	.97	190	4.12
Ce^{4+}	58	.94	190	4.26
Nb^{5+}	41	.69	240	7.5
Ta^{5+}	73	.68	210	7.35

Both elements are markedly lithophile (have a strong affinity for oxygen) and are enriched strongly in the sialic crust of the earth. Because of its physical and crystallochemical properties, Zr^{4+} has restricted entry into the lattice sites of the major rock-forming minerals, hence, relatively few minerals account for the occurrence of most of the zirconium of the earth's outer crust. Approximately 20 well-defined minerals, all of which are classified as silicates or oxides, contain zirconium as an essential constituent. In addition, a large number of minerals contain minor or trace amounts of zirconium in solid solution (Vlasov, 1966a, b; Frondel, 1957). From a quantitative standpoint the mineralogical distribution of zirconium in the earth's outer crust can be almost entirely accounted for by only three minerals: (1) zircon, $ZrSiO_4$; (2) baddeleyite, ZrO_2; and (3) eudialyte, $Na_4(CaFe)_2ZrSi_6O_{17}(OH,Cl)_2$. Because of its widespread occurrence as an accessory mineral in igneous and metamorphic rocks and its concentration in sedimentary rocks (Poldervaart, 1955, 1956; Mertie, 1958; Ronov and others, 1961; Saxena, 1966; Marshall, 1967), zircon is the principal source of zirconium and hafnium.

Baddeleyite occurs in economically important deposits in association with feldspathoidal igneous rocks in the Poços de Caldas Plateau, Minas Gerais, Brazil (Guimarães, 1948; Franco and Loewenstein, 1948). The Poços de Caldas zirconium ore concentrates consisting of baddeleyite and intimately associated zircon (locally called caldasite) contain 0.1–2.0 percent uranium, averaging about 0.5 percent (Tolbert, 1966).

Eudialyte, although considered a relatively rare mineral, occurs in large quantities in some types of potassium- and sodium-rich igneous rocks. It is an essential mineral in a variety of nepheline syenites and nepheline syenite pegmatites of the agpaitic type. (Nepheline syenites in which the molecular ratio $K_2O+Na_2O:Al_2O_3$ is greater than 1 are named agpaitic; nepheline syenites in which the ratio is 1 or less are named miaskitic.) Agpaitic nepheline syenites are known from the Ilimaussaq intrusion in Greenland and the Kola Peninsula in the U.S.S.R. (Gerasimovskii, 1956). In addition to containing deposits of eudialyte, the agpaitic rocks of the Ilimaussaq intrusion contain potential low-grade uranium deposits (Sorensen, 1970a, b) and niobium mineralization (Hansen, 1968).

ABUNDANCE AND DISTRIBUTION IN ROCKS OF THE CRUST

Estimates from recent compilations of the crustal abundance of zirconium and hafnium and of average zirconium and hafnium contents in some of the major rock types of the upper crust are given in table 159. It should be recognized that there are problems inherent in making such estimates of the abundances of elements (Fleischer and Chao, 1960).

TABLE 159.—*Abundances of zirconium and hafnium in terrestrial rocks, in parts per million*

[Data from Brooks, 1969, 1970; Chao and Fleischer, 1960; Degenhardt, 1957; Horn and Adams, 1966; Taylor, 1965; Turekian and Wedepohl, 1961]

Rock type	Zr	Hf	Zr-Hf ratio
Crust	165	3	55
Ultramafic	40	.5	80
Basalt:			
Tholeiitic	50–100	1–2	50
Alkaline	250	3–4	62–83
Syenite	500	10	50
Granodiorite	140	4	35
Granite	180	4	45
Shale	160	3	53
Graywacke	140	2	70
Sandstone	220	5	44
Limestone	20	.5	40
Pelagic clays	150	4	38

Zirconium, a fairly common element, ranking twentieth in order of abundance in the earth's outer crust, is determined routinely in nearly all trace-element investigations. Thus the average zirconium contents of the predominant rock types (background levels) are reasonably well documented and provide a basis for the recognition of zirconium-rich provinces or rock units of potential economic interest. The highly generalized abundance data on igneous rocks (table 159) reflect the well-known tendency for zirconium content to increase in the differentiation sequence ultramafic-mafic-intermediate-felsic, with a particularly marked enrichment in syenitic (alkalic) rocks.

BEHAVIOR OF ZIRCONIUM IN MAGMATIC PROCESSES

The abundance and variation of zirconium in suites of igneous rocks represent different stages of crystallization of magmas (Chao and Fleischer, 1960). Zirconium increases in each stage as differentiation proceeds. The zirconium contents of suites derived from an alkaline base magma are significantly greater than those derived from a basaltic magma of the tholeiitic type. In these rock suites, differentiation produces about a five-fold enrichment in the final products of crystallization. An unusually strong enrichment of zirconium (>1,000 ppm Zr) occurs in the late differentiates of the Skaergaard intrusion in Greenland as compared with the zirconium content of its initial liquid (94 ppm (parts per million)), a value similar to the average zirconium content of tholeiitic basalts (Brooks, 1969). Calc-alkalic and calcic rock suites have the lowest zirconium contents and do not yield differentiates rich in zirconium. The alkalic suites have higher zirconium contents, and zirconium enrichment is most pronounced (>1,000 ppm) in the most siliceous rocks of these suites.

The strong tendency for zirconium to concentrate in rocks with strong alkaline affinities is generally attributed to the greater solubility of zirconium in magmas relatively high in Na, K, F, Cl, and OH. Because of its high ionic potential, zirconium is strongly partitioned into the residual liquid (Ringwood, 1955). Strongly alkalic (pantelleritic) obsidians contain from 1,100–3,000 ppm Zr (Carmichael, 1962), and riebeckite rhyolites and granites from Nigeria have as much as 2,200 ppm Zr (Butler and Thompson, 1965; Bowden, 1966). The contrasting behavior of zirconium in the more calcic suites, which have low contents of alkalis and complexing ions, may thus be attributed for the most part to early crystallization of zircon, which causes only slight to moderate enrichment in the residual magmas.

BEHAVIOR OF HAFNIUM IN MAGMATIC PROCESSES

Data on the hafnium content of rocks are relatively scarce because of the difficulty of determining hafnium in the concentration ranges encountered in rocks. The average content of hafnium in the upper crust of the earth is 3 ppm, approximately one-fiftieth of the abundance of zirconium.

Because hafnium and zirconium are nearly identical in chemical properties, the geochemical behavior of hafnium during magmatic differentiation is quite similar to that of zirconium. In most suites of comagmatic or spatially associated rocks, the Zr–Hf ratios of the bulk rock or zircons are generally between one-half and twice the average Zr–Hf ratio of the earth's crust. Two diabase-granophyre suites from Dillsburg, Pa., and Great Lake intrusion, Tasmania, have absolute and relative enrichment of hafnium in the later-formed rocks. The average Zr–Hf ratio decreased from 68 to 33 in the course of differentiation (Gottfried and others, 1968). In the Skaergaard intrusion, however, the ratio varied in an opposite manner, the enrichment of zirconium and hafnium being accompanied by an increase in the Zr–Hf ratio with differentiation (Brooks, 1969). Limited data on differentiation products of an alkali-olivine basalt indicate an increase in the Zr–Hf ratio from 59 in early formed ankaramite to 85 in more silica- and alkali-rich trachyte (Brooks, 1970).

The geochemical variation of hafnium relative to zirconium in calc-alkaline rocks is based mainly on data obtained on zircon. Analyses for hafnium and the Hf–Zr ratios in zircon from calc-alkaline plutonic rocks indicate about a twofold enrichment of hafnium in zircons from granites over that found in zircon from gabbroic rocks, the Zr–Hf ratio decreasing from 50–70 in the gabbros to 30–35 in the granites. Variations of the Zr–Hf ratios in bulk rock samples from calc-alkaline granitic masses (Condie and Lo, 1971; Esson and others, 1968) are similar to those obtained on zircon. Zircon from undersaturated rocks, such as syenites and nepheline syenites, has low hafnium contents and significantly higher Zr–Hf ratios (60–150) than zircon from ordinary granitic rocks, as shown in table 160. In contrast, zircons with the highest hafnium contents (to 30 percent) and unusually low Zr–Hf ratios (<20) are found in zircon derived from peralkaline granites, granitic pegmatites, and lithium-tantalum-bearing pegmatites (Knorring and Hornung, 1961;

TABLE 160.—*General range of zirconium-hafnium ratios in zircon from igneous rocks*

[Data from Chessex and Delaloye, 1965; Fleischer, 1955; Gottfried and Waring, 1964; Hess, 1962; Lyakhovich and Shevaleyevskii, 1962; Vainshtein and others, 1959]

Rock type	Zr-Hf
Gabbro	50–70
Quartz diorite	40–60
Granodiorite	35–55
Granite (calc-alkalic)	30–45
Granite (alkalic)	20–30
Granite pegmatite	3–20
Nepheline syenite	60–150

Levinson and Borup, 1960; Vainshtein and others, 1959).

TYPES OF DEPOSITS

PRIMARY DEPOSITS

Despite the fact that zircon tends to be enriched in late-stage magmatic differentiates and is a common accessory mineral in many rock types, primary deposits having economic value are rare. An example is the uraniferous zirconium deposits in the Poços de Caldas Plateau, Brazil, which contain baddeleyite and zircon in commercial quantities and yielded an estimated 100,000 metric tons of zirconium ore concentrate before 1953 (Tolbert, 1966). These deposits consist of veins and disseminations of baddeleyite and zircon in nepheline syenite and phonolite of an alkaline intrusive that was emplaced in gneiss and granite in the southwestern part of the Brazilian shield. The veins are believed to be of hydrothermal origin (Tolbert, 1966), but the primary ores may have resulted from lateritic concentration as described by Wedow (1967) for thorium and rare-earth deposits nearby. Concentrations of baddeleyite and zircon were in primary veins disseminated in decomposed bedrock in eluvial deposits on hill slopes, and in alluvial placer deposits along streams and in terraces. Most of the ore production was from placers of alluvial and eluvial origin. Only a small amount was produced from shallow workings along veins. Resources of zirconium ore in the region were estimated to be 50,000–70,000 metric tons which contained 60–85 percent ZrO_2 and about 0.5 percent uranium (Tolbert, 1966).

Other primary deposits are pegmatites which contain rare zirconium minerals or gem-quality zircon, such as those in the Zirconia district, Henderson County, N. C. (Pratt, 1916). Deposits of this type are of little economic significance at present.

SECONDARY DEPOSITS

In the sedimentary cycle, zircon, being heavy (sp gr 4.7) and resistant to chemical decomposition and erosion, is concentrated with other heavy resistate minerals, such as rutile, ilmenite, monazite, and garnet, in placer deposits in stream terraces, along beaches, and in sand dunes. Deposits of this type are the commercial sources of zircon, generally as a coproduct or byproduct of titanium minerals or combinations of other heavy minerals. Examples of commercial zircon-bearing titaniferous sand deposits are Trail Ridge, Fla., and deposits along beaches near the Queensland-New South Wales border, Australia, and along beaches in Western Australia. About 1 ton of zircon is produced for each ton of rutile in concentrates from the Australian deposits (Stamper and Chin, 1970b).

Zircon is also found in small percentages in some phosphatic sediments and in some sand and gravel deposits. Potentially recoverable zircon is usually discarded in waste products from phosphate mining and sand and gravel production. In 1967, for example, 44,000 tons of zircon was discarded along with 60,000 tons of ilmenite and 5,000 tons of monazite as waste products in Florida phosphate operations (Stow, 1968).

Zircon deposits in lithified titanium-rich placers in sandstones or in metamorphosed sandstones are potentially of economic importance. Sandstones of the Precambrian Ocoee Supergroup contain beds having 4.5–9.0 percent zircon (Wedow and Hobbs, 1968).

RESOURCES

IDENTIFIED RESOURCES

The identified resources of zircon are principally in titanium-rich and phosphate-rich sands in placer deposits and in fossil placers in titaniferous sandstone. Resources of baddeleyite in South Africa and Brazil, however, include primary and residual deposits. Data on world resources of zircon are incomplete. Identified zircon resources, in short tons of zircon equivalent, are given in table 161. These resources contain approximately 17 million tons of zirconium and 0.3 million tons of hafnium.

The United States has the world's greatest identified resources of zircon (Stamper and Chin, 1970b). More than 70 percent of the domestic resources are in the Atlantic Coastal States of Florida, Georgia, South Carolina, and New Jersey. The distribution of zircon resources in the United States is shown in table 162. The amount for Florida is modified from published resource data to compensate for estimated production.

The identified resources of zircon in the United States, estimated at 10.8 million tons, contain approximately 5 million tons of zirconium and 0.1 million tons of hafnium. A portion of the resources in

TABLE 161.—*Identified world resources of zircon*

[Identified resources: Specific, identified mineral deposits that may or may not be evaluated as to extent and grade, and whose contained minerals may or may not be profitably recoverable with existing technology and economic conditions. Figures are rounded. NA, not available. Data from Angelli and Chaar (1967), Brazil Dept. Nacional da Produção Mineral (1967), Industrial Minerals (1971), Kauffman (1956), Stamper and Chin (1970b), Tolbert (1966), U.S. Bur. Mines (1969,1972)]

Country	Zircon equivalent, in thousands of short tons
United States	10,800
Australia	8,600
U.S.S.R.	6,000
India	3,360 to 5,000
South Africa, Republic of	2,500
Brazil	2,500+
Ceylon	1,000
Sierra Leone	1,000
New Zealand	400+
Uruguay	136
Argentina	14
Ivory Coast	NA
Japan	NA
Korea	NA
Malagasy Republic (Madagascar)	NA
Malaysia	NA
Nigeria	NA
Thailand	NA
United Arab Republic	NA
Total	36,310+

TABLE 162.—*Identified zircon resources of the United States*

[Identified resources: Specific, identified mineral deposits that may or may not be evaluated as to extent and grade, and whose contained minerals may or may not be profitably recoverable with existing technology and economic conditions. Data from Dow and Batty (1961), Kauffman and Holt (1965), Wessel (1958), Williams (1964)]

State	Zircon resources, in thousands of short tons
Florida	5,400
Georgia	350
North Carolina	22
South Carolina	1,275
New Jersey	1,520
California	1,500
Idaho	280
Montana	94
Wyoming	120
New Mexico	98
Oregon	90
Utah	59
Washington	6
Total	10,814

Florida and Georgia can be considered as reserves. The remainder of the identified zircon resources in the United States is at present not competitive commercially.

HYPOTHETICAL RESOURCES

Hypothetical resources of zirconium and hafnium are difficult to quantify. Untested areas along the coasts of Africa, Asia, and South America, and offshore deposits in shallow waters throughout the world contain concentrations of zircon comparable to those in known deposits. Similarly, fossil placers in sandstone and metasedimentary rocks, and alkalic igneous rocks on all continents contain great quantities of zircon. However, the added cost of mining and separating most hard-rock deposits excludes them from consideration as resources in the near future.

Byproduct zircon and baddeleyite may become increasingly important sources of zirconium and hafnium. Phosphate deposits, such as those mined in Florida (Stow, 1968), and sand and gravel deposits in Alabama and elsewhere in the United States contain substantial amounts of zircon that are potentially recoverable. Baddeleyite-bearing copper ores at Palabora in South Africa (South Africa Mining and Engineering Jour., 1970) currently yield zirconium concentrates in addition to copper, iron, and phosphate products. Many other ores that require grinding and beneficiation contain minor amounts of zirconium minerals that are potentially recoverable.

PROBLEMS FOR RESEARCH

Zircon is currently available in excess of projected demand for the next few decades. Environmental problems such as water pollution and despoilment of beaches, and competitive land use in some areas, may interfere with the production from placer deposits that are worked principally for titanium and byproduct zircon. If the resources in these areas become unavailable, the supply of zircon will be drastically reduced in the United States, and alternate sources will be required.

Research directed toward discovery of alternate sources of zircon is needed. This research should include the search for high-grade primary ores as well as low-grade byproduct or coproduct ores. Sampling and analysis of tailings of various types of beneficiated ores, and sampling of sands in sand and gravel deposits from which washed and sized sand products are currently produced, might disclose potential sources from which zircon can be obtained. Studies of heavy-mineral concentrations in friable sandstone formations in areas where competitive land use and environmental problems are not likely to interfere with mining should also be made. Because of the common association of uranium and thorium with zirconium-bearing minerals, some deposits may be detected by radiometric surveys.

The possibility of recovery of zircon from offshore deposits in shallow waters and of zirconium and hafnium from manganese nodules on the sea floor (Mero, 1972) should also be examined. The recovery of zirconium and hafnium from manganiferous nodules, however, would be completely dependent upon the recovery and processing of the nodules for manganese and other metals and would therefore be a

problem of chemical extraction. Timely research on specific alternate sources of zircon would eliminate the need for future crash programs.

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